Multifunctional Ruthenium Catalysts: A Novel Borohydride-Stabilized Polyhydride Complex Containing the Basic, Chelating Diphosphine 1,4-Bis(dicyclohexylphosphino)butane and Its Application to Hydrogenation and Murai Catalysis

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$[RuCl_2(dcypb)(CO)]_2$ **2** (dcypb = 1,4-bis(dicyclohexylphosphino)butane) was prepared in high yield via phosphine exchange between dcypb and $RuCl_2(CO)(PPh_3)_2(DMF)$ (**1**). Reaction of **2** with 8 equiv of KBH^sBu_3 affords [*fac*-$RuH_3(CO)(dcypb)]^-$ (**3**), stabilized by interactions with a K^+ counterion and an intact KBH^sBu_3 molecule in the third coordination sphere. Substantial ion pairing accounts for the stability and high hydrocarbon solubility of **3**. Complex **3** effects reduction of benzophenone under unprecedentedly mild conditions, at 1 atm of H_2 in refluxing 2-propanol. It is also active for ortho functionalization of benzophenone under 20 atm of ethylene. Stoichiometric experiments reveal facile formation of ortho-metalated $RuH(CO)[OC(C_6H_4)(Ph)](dcypb)$ (**5**), an intermediate proposed in both types of catalysis. The catalytic activity of isolated **5** supports this hypothesis in the case of hydrogenation but not of Murai catalysis. The X-ray crystal structures of **3** and **5** are reported.

Introduction

The catalytic chemistry of ruthenium currently spans an enormous range of processes useful in synthetic organic chemistry. These include hydrogenation and oxidation processes (including epoxidation, aziridination, and dehalogenation), nucleophilic addition to carbon−carbon and carbon−heteroatom bonds, isomerization, and carbon−carbon bond forming reactions such as ring-opening and ring-closing metathesis, acyclic diene metathesis, atom transfer polymerization, cyclopropanation, and Murai coupling, or regioselective formation of C−C bonds at the ortho position of functionalized arenes.[1] Prominent in much of this chemistry are low-valent complexes containing tertiary phosphine ligands. The development of important asymmetrically catalyzed processes, in particular, derives from the ever-increasing number and sophistication of polydentate phosphine ligands, which provide precise control over coordination number and stereochemistry at the metal center.

Despite the potential importance of electronic factors in tuning catalyst reactivity, as exemplified by the increased activity exhibited by an electron-rich metal center in (i.e.) hydrogenation[2] and polymerization[1f] catalysis, low-valent ruthenium complexes containing chelating alkyldiphosphines remain remarkably few, particularly in comparison to the ubiquitous arylphosphines. Of the systems investigated to date, the majority afford chelate rings of five or fewer members on coordination to the metal. Our interest in larger, more flexible chelate complexes is motivated in part by recent observations by ourselves and others in metathesis chemistry,[3−5] in which such species displayed significantly enhanced activity and selectivity relative to four- and five-membered[6] chelates.

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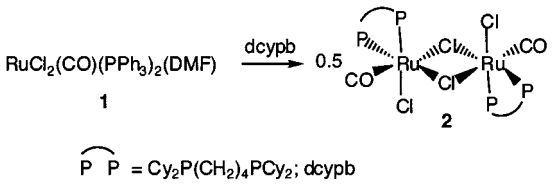
Scheme 1



We recently reported the synthesis of a formerly elusive class of chlororuthenium complexes based on the dcypb ligand (dcypb = $Cy_2P(CH_2)_4PCy_2$).[4] We were interested in the hydride complexes as a point of entry into a range of C−C and C−H activation processes, including hydrogenation,[7] Murai,[1j,8] and metathesis[9] catalysis. In the present work, we describe the synthesis of a novel anionic polyhydride derivative stabilized by bonding interactions with potassium cations and an intact borohydride molecule, and its application to both catalytic reduction and ortho functionalization of benzophenone, processes that afford industrially important organic chemicals and valuable pharmaceutical intermediates.[8,10] We report the synthesis and crystallographic characterization of a complex proposed as an intermediate in both catalytic processes.

Results and Discussion

We recently described the synthesis of N_2-stabilized species $[RuCl_2(dcypb)]_2(N_2)$, in which the dcypb ligand combines steric bulk, basicity, and flexibility.[4] Reactions with CO yielded mononuclear $RuCl_2(dcypb)(CO)_2$, as a mixture of *ccc* and *tcc* isomers: attempts to gain access to monocarbonyl derivatives with potential in catalysis proved unsuccessful. $RuCl_2(CO)(PPh_3)_2(DMF)$[11] (**1**), containing a preinstalled carbonyl ligand, provides a convenient precursor to such species. Thus, reaction of **1** with 1 equiv of dcypb effects clean transformation into $[RuCl_2(dcypb)(CO)]_2$ (**2**), in ca. 90% yield. The complex is assigned the geometry shown in Scheme 1 on the basis of microanalytical and $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR data. The dinuclear formulation is supported by electrospray mass spectrometric data, which shows the molecular ion minus one chloride. A pair of ^{31}P NMR doublets (δ_P 50.8, 42.5; $^2J(PP)$ = 23 Hz) indicates the presence of inequivalent phosphines, while the triplet for the carbonyl ligand confirms that this ligand is cis to two phosphine groups (δ 200; $^2J(PC)$ = 15 Hz). A single infrared ν(CO) band is present. In contrast, a dtbpe analogue (dtbpe = $Bu^t_2PCH_2CH_2PBu^t_2$) exhibits two independent ^{31}P NMR singlets, on the basis of which it was proposed to exist as cisoid- and transoid-CO isomeric forms, in which the chelating diphosphine is coplanar with the bridging chloride ligands.[12]

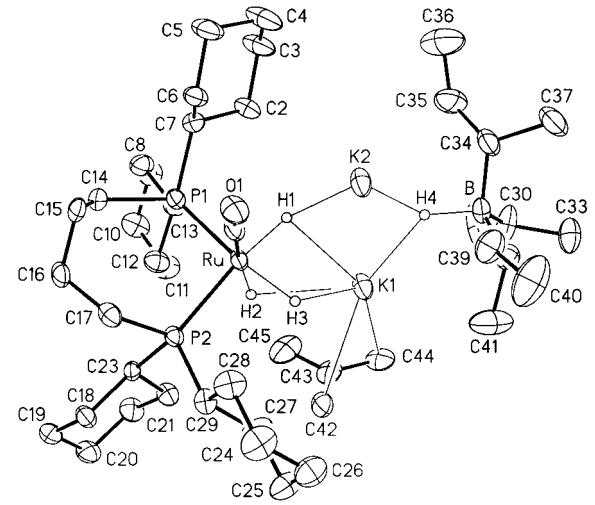
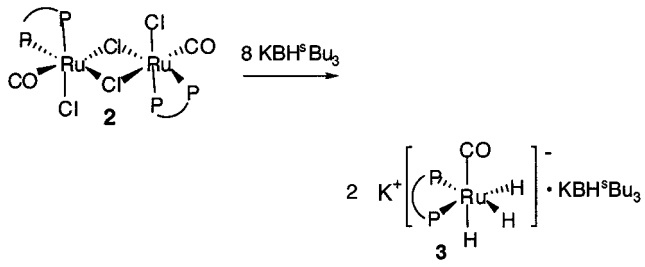


Figure 1. Molecular structure and atomic numbering of K[*fac*-RuH_3(dcypb)(CO)]KBH^sBu_3·0.5(toluene) (**3**). Thermal ellipsoids are depicted at the 30% probability level; nonmetal hydrogens are omitted for clarity.

Scheme 2



Transition-metal hydrides are commonly prepared by reaction of halide (or hydrido halide) precursors with alkali-metal hydrides in tetrahydrofuran. Use of potassium tri-*sec*-butylborohydride as a soluble hydride reagent offers a stoichiometrically precise alternative. Reaction of **2** with 2, 4, or 6 equiv of KBH^sBu_3 afforded a single phosphorus-containing product (**3**; δ_P 59.3 (s), THF), accompanied by unreacted **2**. We found complete transformation only on use of 8 equiv of hydride (Scheme 2). The structure of **3** was elucidated by NMR and IR spectroscopy and X-ray diffraction (Figure 1). Several minor products, which were not identified, were detected by ^{31}P NMR on use of <8 equiv of KBH^sBu_3 in benzene. That these are due to irreversible decomposition in the absence of excess borohydride in this solvent is indicated by clean transformation of **2** to **3** on use of 8 equiv of KBH^sBu_3, but not on *sequential* addition of borohydride (2 × 4 equiv) to the benzene solution.

The requirement for "excess" hydride is due in part[13] to formation of an anionic trihydride species, examples of which have been reported in Ru and Os systems containing trans-disposed P^iPr_3 or cis-PMe_2Ph ligands.[14,15] Consistent with formation of [*fac*-RuH_3(dcypb)(CO)]$^-$ is the appearance of two hydride signals, in a 2:1 ratio, by ^1H NMR; the cis geometry of the

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(13) Observation of apparently unreacted KHB^sBu_3 (spectroscopically detected in the product oil; δ_H −1.0; ν(B−H) 1901 (m) cm^{-1}) was initially puzzling, as was the required stoichiometry. Both are accounted for by the presence of a stabilizing interaction between a Ru−H bond and the potassium ion of an intact KHB^sBu_3 molecule (see text).

chelating diphosphine in **3**, coupled with the destabilizing influence of a *trans*-dihydride geometry,[16] precludes formation of a *mer*[14] isomer. The hydride signals comprise the AA′B component of a AA′BXX′ spin system. The upfield portion (H_A, $H_{A'}$) is a second-order multiplet, with a pattern identical with that previously shown for the magnetically inequivalent hydride ligands in [K(1-aza-18-crown-6)][*fac*-$OsH_3(CO)(P^iPr_3)_2$][14] and K[*fac*-$RuH_3(PPh_3)_2$].[17] The downfield hydride signal H_B appears as a broadened, distorted triplet, from which the P−H coupling constant can be extracted (δ_H −9.29, $^2J(HP_{cis}) = 22$ Hz). In the previously reported systems, H_B appears as a triplet of triplets.[14,17] The H−H couplings are not resolved in **3**, but decoupling of the phosphorus signal permits measurement of a ^2J(HH) value of 4.8 Hz for this signal. A single hydride stretching band (1834 cm^{-1}) is present in the infrared spectrum.

Efforts to confirm the presence of the presumed potassium counterion by microanalysis were frustrated by the high solubility of **3** and its tendency to form oils, which hampered separation from boron and potassium byproducts. Small amounts of **3** were isolated as a fine powder from cold pentane but underwent decomposition on drying under high vacuum. We earlier reported exhaustive dehydrogenation of the dcypb ligand on exposure of $[RuCl_2(dcypb)]_2(N_2)$ to vacuum.[4] Such behavior appears to be general for labile or coordinatively unsaturated dcypb[4,18] or PCy_3[19] complexes of ruthenium and may also be a feature of the P^iPr_3 systems.[14]

Crystal Structure of 3. Storage of **3** as an oil at room temperature resulted in serendipitous formation of crystals suitable for X-ray analysis. Selected bond distances and angles are listed in Table 1. The crystal structure (Figure 1) shows a $[RuH_3(PP)(CO)]^-\cdots K^+\cdots KBH^sBu_3$ entity, in which the Ru center possesses the *fac* geometry deduced spectroscopically, and the potassium counterion interacts with all three hydride ligands (located and refined with a riding model), as well as a solvating toluene molecule. The Ru-based anion in **3** is a distorted octahedron, in which the P−Ru−P angle of 100.51(7)° indicates compression of the hydride face. This angle, and the average Ru−H distance of 1.63(3) Å, are comparable to features present in [K(18-crown-6)][*fac*-$H_3Ru(PPh_3)_3$].[20]

More unexpected is the presence in **3** of a "solvating", intact KBH^sBu_3 molecule, the K^+ ion of which is associated with a ruthenium-based hydride, the boron hydride, and the carbonyl oxygen of a neighboring Ru molecule (for $CO\cdots K^+$ interaction, see Figure 2). While examples of transition-metal−borohydride interactions are well established and in some cases afford isolable species,[21] this is, to our knowledge, the first crystallographically characterized example of a metal hydride stabilized by an intact borohydride molecule within the third coordination sphere. Tight hydride−K^+ ion pairing (vide infra), in conjunction with shielding of the potassium ions by *sec*-butyl, cyclohexyl, and (for K(1)) toluene groups, renders the entire complex highly lipophilic, resulting in extreme solubility in hydrocarbon solvents, including pentane. This effect is reminiscent of Caulton's observation of high hydrocarbon solubility in $K_2Os_2H_6(PMe_2Ph)_6$, in which the potassium counterions are enfolded by two phosphine phenyl rings in a centrosymmetric dimer.[15] The stoichiometric requirements noted earlier imply that interactions with *both* K^+ and KBH^sBu_3 are necessary to stabilize the anionic tri-

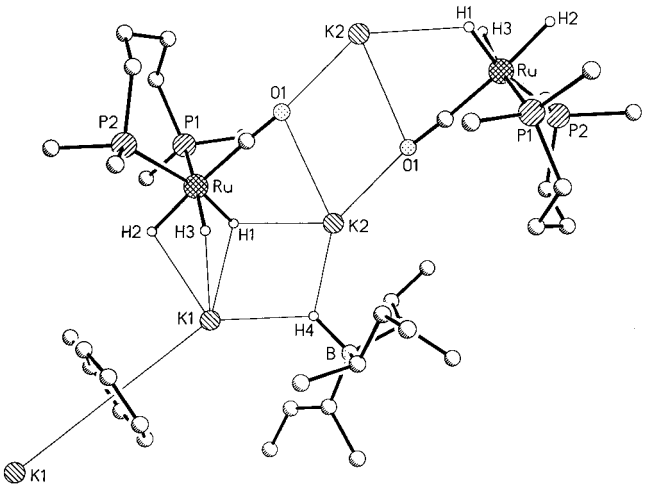

Figure 2. Schematic diagram illustrating the position of K^+ ions within the packing of K[*fac*-RuH_3(dcypb)(CO)]-KBH^sBu_3·(toluene) (**3**) units. Cyclohexyl groups are abbreviated to a single carbon for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 3

Bond Distances			
Ru−P(1)	2.335(2)	B−H(4)	1.32(6)
Ru−P(2)	2.3375(19)	K(1)−C(42)	3.251(8)
Ru−C(1)	1.807(7)	K(1)−C(43)	3.197(7)
Ru−H(1)	1.63(3)	K(1)−C(44)	3.260(7)
Ru−H(2)	1.64(3)	K(2)−O(1)#2	2.650(5)
Ru−H(3)	1.63(3)	K(2)−O(1)#1	3.103(5)
O(1)−C(1)	1.201(7)	Ru−K(1)	3.3998(17)
K(1)−H(1)	2.63(5)	Ru−K(2)	3.5337(16)
K(1)−H(3)	2.64(5)	B−K(1)	3.577(8)
K(2)−H(1)	2.82(5)	B−K(2)	3.284(8)
K(1)−H(2)	2.67(5)	B−C(30)	1.656(11)
K(2)−H(4)	2.44(6)	B−C(34)	1.645(11)
K(1)−H(4)	2.57(6)	K(1)−K(2)	3.937(2)
Bond Angles			
P(1)−Ru−P(2)	100.51(7)	Ru−K(2)−K(1)	53.81(3)
C(1)−Ru−P(1)	98.8(2)	Ru−K(1)−K(2)	57.02(3)
C(1)−Ru−P(2)	90.9(2)	Ru−C(1)−K(2)	92.5(3)
O(1)−C(1)−Ru	175.0(6)	C(34)−B−K(1)	131.2(5)
C(1)−Ru−K(1)	123.4(2)	C(34)−B−K(2)	74.6(4)
C(1)−Ru−K(2)	56.8(2)	C(14)−P(1)−Ru	118.8(2)
P(1)−Ru−K(1)	117.01(6)	C(17)−P(2)−Ru	113.3(2)
P(2)−Ru−K(1)	120.76(5)	C(7)−P(1)−Ru	114.6(2)
P(1)−Ru−K(2)	112.29(6)	C(13)−P(1)−Ru	117.5(2)
P(2)−Ru−K(2)	136.03(6)	C(23)−P(2)−Ru	120.8(2)
K(1)−Ru−K(2)	69.17(4)	C(29)−P(2)−Ru	116.7(2)
Ru−K(1)−B	108.58(14)	C(30)−B−K(1)	82.1(4)
B−K(2)−Ru	112.35(15)	C(30)−B−K(2)	146.9(5)

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Table 2. Reduction of Benzophenone to Benzhydrol[a]

entry	catalyst	$p(H_2)$ (atm)	solvent	conversion (%)
1	**4**	8	^{i}PrOH	99[b,c]
2	**3**	8	C_6H_6	100[b]
3	**3**	2	C_6H_6	67
4	**3**	1	^{i}PrOH	96
5	**3**	0	^{i}PrOH	55
6	**5**	1	^{i}PrOH	95
7	**5**	1	^{i}PrOH	90[d]

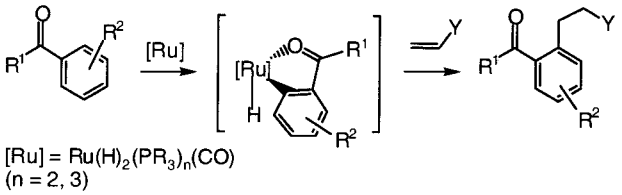
[a] Reactions were carried out at 60 °C for 24 h, using 0.34 mM [Ru]; $[Ph_2CO]$:[Ru] = 3000:1, unless otherwise stated. [b] Reaction at 35 °C for 18 h. [c] Reference 10. [d] Reaction using 100 g (0.55 mol, 2.75 M) of benzophenone ([Ru] = 0.138 mM; $[Ph_2CO]$:[Ru] = 20 000:1) at reflux for 3 h; acetone removed by distillation after 1 h.

hydride complex (the former alone is insufficient, as indicated by decomposition of **3** on use of 6 equiv of borohydride in benzene; see above).

A portion of the ion-pair structure for **3** is shown in Figure 2. Bridging interactions between K(2) and the carbonyl oxygens are present in one dimension, with sandwiching of a toluene molecule between adjacent K(1) cations in a second. Interaction of metal cations with a carbonyl oxygen is common in hydridocarbonylmetalates;[22] occupation of this site by K(2) in **3** leaves K(1) free to bind the hydride face. Potassium−carbon distances (3.20−3.26 Å) are comparable with other arene−K^+ interactions.[15,23] Two distinct crystallographic inversion centers are present. The K(2) ion and its symmetry-generated pair are bridged by a carbonyl oxygen, with an interatomic separation of 4.679(2) Å, while a second inversion center is located at the center of the toluene molecule coordinated to K(1), with a K···(centroid) distance of 3.015(2) Å, or an effective K···K distance of 6.030(2) Å. The closest K···K interatomic separation, 3.937(2) Å, occurs between the symmetry-unique K(1) and K(2) ions bridged by the borohydride anion. The potassium ion K(1) is approximately equidistant between Ru−H and B−H entities, with K···H distances ranging from 2.57(6) to 2.67(5) Å, while K(2) is more closely associated with the borohydride B−H (K(2)···H(4), 2.44(6) Å; K(2)···H(1), 2.82(5) Å). Intimate potassium−hydride ion pairing in both the second and the third coordination spheres is indicated by these values: cf. distances of 2.52−3.02 Å for the tight ion pair in $[KH_3Os(PMe_2Ph)_3]_2$.[15]

Catalysis. The hydrogenation activity of **3** (Table 2) compares favorably with that of the important Noyori systems containing chelating diphosphine and 1,2-diamine ligands.[1k] Thus, **3** effects reduction of benzophenone at *1 atm* of H_2 and 60 °C in 2-propanol, in comparison to the requirement for H_2 pressures of 8 atm using $RuCl_2[P(C_6H_4\text{-}4\text{-}CH_3)_3]_2(NH_2CH_2CH_2NH_2)$ **4** (entries 1 and 4).[10] The exceptionally high hydrogenation activity of **3** is retained on a large scale (entry 7), with reduction of 100 g of benzophenone (2.7 M ketone, [S]:[C] = 20 000:1) via intermediate **5** (vide infra) reaching 48% conversion within 1 h (TOF = 9600 h^{-1}). When the acetone byproduct is distilled off,[24] 90% conversion is attained within a further 2 h.

Scheme 3



Hydrogenation via **3** proceeds in both aromatic and 2-propanol solvent, the latter being associated with higher activity, possibly owing to protonation of the trihydride to generate catalytically active $[RuH_2(H_2)(dcypb)(CO)]$.[25] Both H_2 hydrogenation and transfer hydrogenation pathways are accessible for **3**, as indicated by partial retention of activity in 2-propanol under N_2 (entry 5). Efficient transfer hydrogenation of benzophenone under Ar or N_2 was previously reported, albeit at much higher catalyst loadings (0.1−0.5 mol % of Ru, vs 0.005 mol % for **3**).[26,27] The very high activity of **3** is particularly notable, given the emerging view that an NH group in the ligand set is required for efficient ketone hydrogenation.[1k,24] Very recently, Gimeno and co-workers reported that phosphine−imine ligands devoid of an NH functionality performed better than phosphine−2° amine ligands in the transfer hydrogenation of ketones.[28]

The hydrogenation activity of **3** prompted us to undertake a preliminary evaluation of its activity for ortho functionalization of aromatic ketones (Scheme 3), for which an ortho-metalated intermediate[1j,8,29] is proposed similar to that described[25] for benzophenone hydrogenation. First described by Murai less than 10 years ago, such C═C/CH coupling reactions are much less developed than hydrogenation catalysis.[1j,8] Relatively few variants on the original $Ru(H)_2(CO)(PPh_3)_3$ catalyst systems have been explored, though a recent breakthrough described room-temperature coupling using $Ru(H)_2(H_2)_2(PCy_3)_2$ as the precursor.[30] We were intrigued by the potential Murai activity of systems containing the "RuH_2(PP)" (PP = chelating dialkylphosphine) structural motif, as loss of monodentate phosphine has emerged as a potentially important contributor to deactivation pathways.[31] Complex **3** shows modest activity but improved stability over the PCy_3 systems, which were unstable at elevated temperatures. Thus, 58% conversion of benzophenone to 2-ethylbenzophenone is found after 22 h at 60 °C under 260 psi of ethylene (1.5 mM **3**; 23.7 mM Ph_2CO).

Identification of a Catalytic Intermediate. ^{31}P NMR analysis of catalyst solutions following hydrogenation revealed a single species, identified as RuH[*o*-C(O)-

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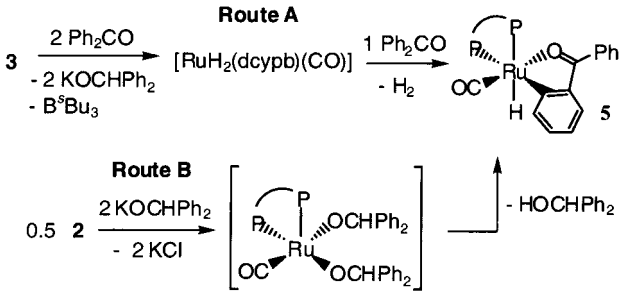
Scheme 4[a]



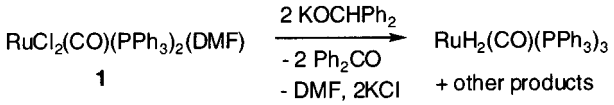
[a] One of the two enantiomeric forms of **5** is shown.

$(Ph)C_6H_4](dcypb)(CO)$ (**5**) on the basis of NMR, XRD, and elemental analysis. In stoichiometric experiments, **3** was completely converted to **5** in the presence of a 3-fold excess of benzophenone (Scheme 4, Route A), 2 equiv of the ketone being converted to $KOCHPh_2$ (δ_H 5.67, C_6D_6). No benzhydrol (Ph_2CHOH; δ_H 5.49 (d, $^3J(HH) = 3.6$ Hz), C_6D_6) was observed by ^1H NMR or IR spectroscopy, but a peak for dissolved H_2 was present for reactions carried out in a sealed system, implying the reaction sequence depicted. We saw no evidence of the presumed $RuH_2(dcypb)(CO)$ intermediate, in contrast to the corresponding reaction of $K[fac\text{-}RuH_3(PPh_3)_3]$, in which the greater steric protection afforded by the *trans*-PPh_3 ligands permitted observation of $RuH_2(PPh_3)_3$ en route to $RuH[o\text{-}C(O)(Ph)C_6H_4](PPh_3)_3$.[25b] We identify the ortho proton of benzophenone as the origin of the hydride ligand in **5**, rather than the hydride originally present in **3**, on the basis of a labeling experiment in which benzophenone was reacted with trideuteride **3-*d*$_3$** (itself prepared by treating **2** with 8 equiv of $LiDBEt_3$). A hydride signal corresponding to that originally observed for **5** (δ_H −6.32) was observed, which integrated 1:1 against an isolated aromatic proton of the benzophenone ligand.

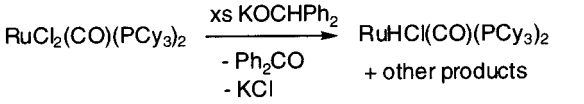
Structure **5** represents a resting state in the catalytic hydrogenation of benzophenone via **3**, as indicated by the observation of approximately identical activity for catalysis via isolated **5** (Table 2, entry 6). Its PPh_3 analogue has been proposed as a key intermediate in the ortho functionalization of benzophenone.[8,29] However, the markedly lower Murai activity of **5** vs that of **3** (26% vs 58% under the conditions above) suggest that the ortho-metalated species is not on the reaction coordinate for Murai coupling but is in fact a catalytic *sink* in this chemistry.[32] We note the possibility that the observed activity of **5** may arise from the reversibility of Ru insertion into the ortho C−H bond.[8b]

Direct reaction of **2** with $KOCHPh_2$ (Scheme 4, route B) provides a cleaner and more efficient route to **5**. Formation of **5** by either method is signaled by a color change from yellow to red. Although the transformation is quantitative, as judged by ^{31}P NMR, high solubility limits isolated yields of **5** to 51%. A doublet of doublets in the hydride region of the ^1H NMR spectrum (δ −6.3; $^2J(HP_{trans}) = 90$ Hz; $^2J(HP_{cis}) = 24$ Hz), signifies the presence of a hydride ligand trans to one phosphorus nucleus and cis to the other. Consistent with this is the $^{31}P\{^1H\}$ NMR spectrum, which shows a pair of doublets (δ 25.7, 30.5; $^2J(PP) = 20$ Hz). $^{31}P-^1H$ HMQC experiments correlate the upfield phosphorus resonance with an aromatic proton that appears as a doublet of doublets (9.00 ppm O−CH of metallated ring). In the $^1H\{^{31}P\}$ NMR spectrum, the latter collapses to a doublet, and the hydride signal collapses to a singlet. In conjunction with the $^{13}C\{^1H\}$ NMR data, which shows a new quaternary carbon signal far downfield (δ_C 215), as a doublet of doublets split by cis and trans phosphines, this provides unambiguous evidence for ortho-metalation of the benzophenone ligand. A triplet for the CO ligand is also seen. An infrared band of medium intensity appears for Ru−H (1859 cm^{-1}), accompanied by a weak band for the carbonyl functionality within the η^2-O=C(Ph)(C_6H_4) ligand and a strong band for the CO ligand (1580, 1900 cm^{-1}). The low energy of the ketonic band is consistent with chelation of the ketone.[33] Related complexes containing monodentate phosphines have been described in other work.[25,30,32,34]

Scheme 5



Scheme 6



One equivalent of Ph_2CHOH is evolved in the formation of **5** via **2**, suggesting that reaction proceeds via reductive elimination of alcohol from a bis(alkoxide) intermediate (Scheme 4, route B). In contrast, we find that reactions of monodentate phosphine analogues **1** and $RuCl_2(CO)(PCy_3)_2$ with $KOCHPh_2$ involve β-elimination of benzophenone (and disproportionation in the case of **1**), terminating in Ru hydride complexes (Schemes 5 and 6). The principal products were $RuH_2(CO)(PPh_3)_3$ and $RuHCl(CO)(PCy_3)_2$ (for the PPh_3 and PCy_3 reactions, respectively); in both cases unidentified side products were also observed. Both hydride species were identified by their characteristic NMR spectra.[35,36]

X-ray Crystal Structure of 5. Crystals of **5** suitable for X-ray analysis were obtained by slow concentration from toluene solution (Figure 3). Selected bond distances and angles are listed in Table 3. This structure is the first crystallographically characterized example of a Ru−hydride complex containing ortho-metalated benzophenone; related chloride-containing species, including acetophenone derivatives, have been reported in other chemistry.[32,34,37] The five-membered metallacycle in **5** constrains significant deviations from regular

(32) Following submission of this paper, a report of ortho-metalated Ru−acetophenone complexes of the general formula $RuH(o\text{-}C_6H_4C(O)CH_3)(L)(PPh_3)_2$ (L = PPh_3, CO, DMSO) was published: Jazzar, R. F. R.; Mahon, M. F.; Whittlesey, M. K. *Organometallics* **2001**, *20*, 3745. In contrast to the behavior of **5**, the CO derivative was found to be completely inactive for Murai coupling. X-ray structural characterization of this complex locates the hydride ligand in the Ru-O−C(aryl) plane (cf. the structure of **5** in Figure 3).

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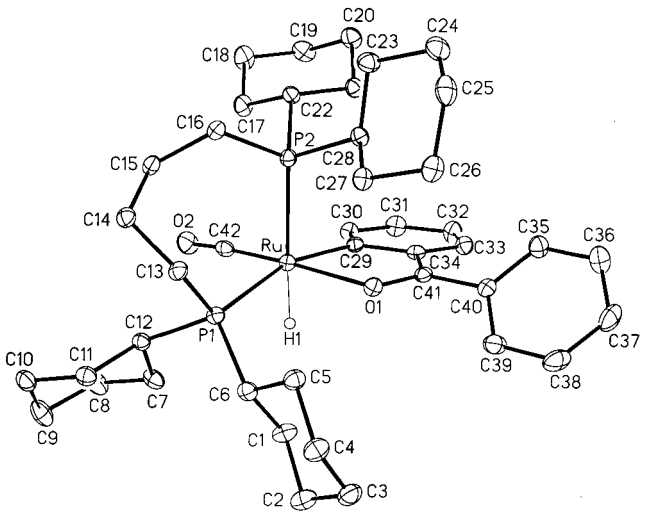

Figure 3. Molecular structure and atomic numbering of RuH(CO)[OC(Ph)(C_6H_4)(dcypb)] (**5**). Thermal ellipsoids are depicted at the 30% probability level; nonmetal hydrogens are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 5

	Bond Distances		
Ru−P(1)	2.3753(9)	O(1)−C(41)	1.259(3)
Ru−P(2)	2.4237(8)	O(2)−C(42)	1.166(3)
Ru−C(42)	1.814(3)	P(1)−C(13)	1.846(3)
Ru−C(29)	2.056(3)	P(1)−C(12)	1.859(3)
Ru−O(1)	2.144(2)	P(2)−C(16)	1.858(3)
Ru−H(1)	1.48(2)	P(2)−C(28)	1.861(3)
	Bond Angles		
P(1)−Ru−P(2)	99.44(3)	C(28)−P(2)−Ru	115.43(10)
C(42)−Ru−P(1)	91.09(10)	C(12)−P(1)−Ru	113.17(10)
C(42)−Ru−P(2)	96.11(9)	C(6)−P(1)−Ru	116.44(10)
O(1)−Ru−P(2)	90.27(5)	C(28)−P(2)−Ru	115.43(10)
O(1)−Ru−P(1)	94.13(6)	C(22)−P(2)−Ru	116.46(10)
C(16)−P(2)−Ru	117.99(9)	O(2)−C(42)−Ru	176.8(3)
C(13)−P(1)−Ru	119.42(10)		

octahedral geometry; the O(1)−Ru−C(29) angle of 77.24(10)°, in particular, is highly compressed relative to the ideal value of 90°, as also found in [Ru(CO)-{$C_6H_3MeC(O)C_6H_4Me$}Cl(PMe_2Ph)$_2$] (**6**).[34] The fused five- and six-membered rings in **5** are coplanar, while the nonmetalated ring is tilted ca. 45° out of this plane, relieving the interaction between the hydrogen atoms on C(33) and C(35). The P−Ru−P bite angle (99.44(3)°) is close to that observed for **3**, a consequence of the steric demand of the dcypb ligand.[4] The Ru−C(29) bond length for the ortho-metalated carbon trans to phosphine is marginally longer than that observed for **6**, in which the trans position is occupied by a chloride ligand (2.056(3) Å for **5**, vs 1.987(19) and 2.044(17) Å for the two independent molecules in the asymmetric unit for **6**).

Conclusions

The foregoing describes a general route into the chemistry of monocarbonyl ruthenium complexes containing the basic, bulky diphosphine dcypb. Dimeric [$RuCl_2$(dcypb)(CO)]$_2$ (**2**) provides a synthetically valuable precursor to key catalytic species, including the novel, anionic trihydride K[RuH_3(PP)(CO)]·KBH^{s}Bu$_3$ (**3**). Like other dcypb complexes, **3** is susceptible to decomposition in the absence of stabilizing interactions, provided in **3** by H···K^+ and CO···K^+ interactions involving the potassium counterion and an intact borohydride molecule in the third coordination sphere. Restraint of decomposition permits us to redirect the heightened reactivity of **3** toward the challenging problems of catalytic hydrogenation and ortho functionalization of benzophenone. Exceptionally high activity is found in hydrogenation, permitting reduction at 1 atm of H_2. An ortho-metalated intermediate implicated in catalytic hydrogenation was identified and crystallographically characterized: this structural form represents a catalytic sink in Murai chemistry. Current efforts utilizing **3** and related species show considerable promise for *tandem* Murai−hydrogenation reactions, a potentially valuable route to pharmaceutically relevant benzhydrol derivatives.

Experimental Section

General Procedures. All reactions were carried out under N_2 using standard Schlenk or drybox techniques, unless otherwise noted. For reactions above 2 atm, hydrogen (Praxair UHP Grade) was used as received; for reactions at or below 2 atm, H_2 was purified by passage through a Deoxo cartridge and an indicating Drierite column in series. Ethylene (Praxair, instrument grade) 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. C_6D_6 and toluene-d_8 (Cambridge Isotopes) were dried over activated sieves (Linde 4 Å) and degassed by consecutive freeze/pump/thaw cycles. $RuCl_2(PPh_3)_2$(CO)(DMF) (**1**),[11] RuHCl(CO)(PCy_3)$_2$,[35] and dcypb[38] were prepared as previously described. PCy_3 was purchased from Strem and used without further purification. $KOCHPh_2$ was prepared by reaction of benzhydrol with KH. Super-Deuteride (lithium triethylborodeuteride; 1.0 M solution in THF) and potassium tri-*sec*-butylborohydride (1.0 M solution in Et_2O) were purchased from Aldrich and used without further purification. ^{1}H NMR (200 or 300 MHz) spectra were recorded on a Varian Gemini 200 or Bruker Avance-300 spectrometer; ^{31}P NMR (121 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on the 300 MHz instrument. IR spectra were measured on a Bomem MB100 IR spectrometer. Microanalyses were carried out in house, using a Perkin-Elmer Series II CHNS/O instrument, or by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

Preparation of Ru_2Cl_4(dcypb)$_2$(CO)$_2$ (2). A solution of dcypb (520 mg, 1.15 mmol) in 10 mL of CH_2Cl_2 was added to a suspension of $RuCl_2$(CO)(PPh_3)$_2$(DMF) (**1**; 925 mg, 1.16 mmol) in 35 mL of CH_2Cl_2. The mixture was stirred at ambient temperature for 18 h and then stripped of solvent. Addition of benzene to the yellow oil caused deposition of crystals of **2** over 2 h. The product was filtered, washed with C_6H_6 (2 mL), Et_2O (4 × 2 mL), and then hexanes (5 × 2 mL), and dried under vacuum. Yield: 0.665 g (88%). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 50.8 (d, ^2J(PP) = 23 Hz), 42.5 (d, ^2J(PP) = 23 Hz). ^{1}H NMR ($CDCl_3$, δ): 1.10−2.53 (br, CH_2, Cy of dcypb). ^{13}C{^{1}H} NMR (C_6D_6, δ): 200.3 (t, ^2J(CP) = 15 Hz, *C*O). IR (Nujol; cm^{-1}): ν(CO) 1958. Anal. Calcd for $C_{29}H_{52}Cl_2OP_2Ru$: C, 53.53; H, 8.06. Found: C, 53.36; H, 7.89. ESI-MS (*m*/*z*): calcd for $C_{58}H_{104}Cl_4O_2P_4Ru_2$ (M^+), 1300.6; found {M − Cl + H}, 1267.1.

Preparation of K[Ru(dcypb)(CO)H$_3$]·KBH^{s}Bu$_3$ (3). A suspension of **2** (0.300 g, 0.46 mmol of Ru) in 15 mL of C_6H_6 was stirred as potassium tri-*sec*-butylborohydride (1.84 mL of a 1.0 M solution) was injected. The yellow solution was stirred

(38) Chau, D. E. K. Y. M.Sc. Thesis, University of British Columbia, 1992.

at ambient temperature for 15 h and then stripped of solvent. The resulting oil was taken up in pentane. Cooling the solution to −35 °C gave small amounts (14 mg) of **3** as a pale yellow powder. Attempts to dry the precipitate under vacuum for microanalysis caused decomposition to many ^{31}P-containing species (NMR). The filtrate was stripped to a yellow oil, which could not be purified. X-ray-quality crystals were obtained from a sample of the oil that was subsequently dissolved in toluene and then stripped again. Crystals of **3** (as a toluene solvate) deposited from the oil over 2 days at room temperature. Spectroscopic characterization was carried out on the mixture of crystals and oil. ^{31}P{^{1}H} NMR (C_7D_8, δ): 54.7 (s). ^{1}H NMR (C_7D_8, δ): 0.21−2.04 (br, CH_2, Cy of dcypb; ^{s}Bu), −1.01 (br, 1 H, B*H*), −9.29 (br t, 1 H, Ru*H*, ^2J(HP$_{cis}$) = 22 Hz), −10.32 (m, 2 H, Ru(*H*)$_2$). ^{1}H{^{31}P} NMR: −9.2 (t, Ru*H*, ^2J(HH) = 4.8 Hz), −10.31 (br s, Ru(*H*)$_2$). Hydride T_1 (min, 263 K, 300 MHz): δ −9.29, 208 ms; δ −10.32, 279 ms. ^{13}C{^{1}H} NMR (C_6D_6, δ): 213.7 (t, *C*O, ^2J(CP) = 7.7 Hz). IR (neat; cm^{-1}): ν(CO) 1916 (m), ν(BH) 1901 (m), ν(RuH) 1834 (s).

Preparation of RuH(CO)[OC(Ph)(C_6H_4)](dcypb) (5). (a) Via 3. A suspension of **2** (100 mg, 0.15 mmol Ru) in 4 mL of C_6H_6 was stirred as potassium tri-*sec*-butylborohydride (0.616 mL of a 1.0 M solution) was added quickly via syringe. The yellow solution was stirred at ambient temperature for 15 h to give **3**, following which benzophenone (84.2 mg, 0.46 mmol) was added to give a red solution. After a further 5 h, the solvent was reduced to 0.5 mL under vacuum and diethyl ether (10 mL) was added. The solution was filtered through neutral alumina and then concentrated to 2 mL. Microcrystalline **5** precipitated on cooling to −35 °C over 15 h. The dark red crystals were filtered and washed with cold Et_2O (2 × 1 mL), followed by cold pentane (4 × 1 mL). The isolated yield of spectroscopically clean **5** was 60 mg (51%); the low yield is incurred by the solubility of **5** (see text). The product was recrystallized from benzene/pentane. Experiments carried out on an NMR scale in C_6D_6 showed a ^{1}H NMR singlet (5.67 ppm) for KOCHPh$_2$; no benzhydrol was observed by NMR or IR. ^{31}P-{^{1}H} NMR (C_6D_6, δ): 25.7 (d, ^2J(PP) = 20 Hz), 30.5 (d, ^2J(PP) = 20 Hz). ^{1}H NMR (C_6D_6, δ): 9.00 (dd, 1 H, *o*-CH of ortho-metalated ring, ^3J(HH$_{ortho}$) = 7.7 Hz, ^4J(HP) = 4.1 Hz), 7.85 (d, 1 H, Ph, J(HH) = 8.1 Hz), 7.65 (m, 2 H, Ph), 7.09 (m, 4 H, Ph), 6.79 (t, 1 H, Ph, J(HH) = 7.5 Hz), 0.53−2.60 (m, CH_2, Cy of dcypb, 52 H), −6.32 (dd, 1 H, Ru*H*, ^2J(HP$_{trans}$) = 86.7 Hz, ^2J(HP$_{cis}$) = 24.3 Hz). ^{13}C{^{1}H} NMR (C_6D_6, δ): 215.4 (dd, Ru*C*, ^2J(CP$_{trans}$) = 66 Hz, ^2J(CP$_{cis}$) = 6.5 Hz), 212.1 (t, Ru*C*O, ^2J(CP) = 8.1 Hz), 205.3 (dd, Ru−O═*C*, ^3J(CP) = 7.4 Hz, ^3J(CP) = 3.1 Hz). IR (Nujol; cm^{-1}): ν(CO) 1900 (s), ν(RuH) 1859 (m), ν(CO; ketonic) 1580 (w). Anal. Calcd for $C_{42}H_{62}O_2P_2Ru$: C, 66.20; H, 8.20. Found: C, 66.67; H, 7.94.

(b) Via 2 (NMR Scale). Addition of KOCHPh$_2$ (14 mg, 0.061 mmol) in 0.3 mL of C_6D_6 to a stirred suspension of **2** (20 mg, 0.031 mmol Ru) in 0.4 mL of C_6D_6 caused dissolution and a color change from yellow to dark red. Stirring was continued for 1 h, after which PPh$_3$ (8.1 mg, 0.031 mmol) was added as an integration standard. ^{31}P NMR: **5** (100%). ^{1}H NMR: **5** + Ph$_2$CHOH (1:1 ratio); δ(Ph$_2$CHOH) 7.60−7.15 (m, 10 H, Ph), 5.49 (d, 1H, C*H*, J_{HH} = 3.6 Hz). The hydroxyl O*H* peak (δ 1.76) is obscured by the cyclohexyl resonances of **5**.

Deuterium-Labeling Experiment: Preparation of 3-d_3 and Its Reaction with Benzophenone. A suspension of **2** (20 mg, 0.031 mmol) in C_6D_6 (0.7 mL) was stirred as Super-Deuteride (120 μL of a 1.0 M solution) was added. The yellow solution was stirred at ambient temperature for 15 h. ^{31}P NMR showed the expected broad singlet at 54.3 ppm; an unidentified byproduct (<10% of total integrated intensity) was also apparent at 61.1 ppm. ^{1}H NMR confirmed formation of **3-d_3**. Benzophenone was added (22 mg, 0.12 mmol), and the reaction mixture was stirred at room temperature. ^{31}P NMR analysis after 2 h confirmed formation of **5**. ^{1}H NMR analysis showed a spectrum identical with that reported for **5** above, in which the hydride signal at −6.32 ppm was integrated as 1:1 vs an isolated, ortho aromatic proton at 9.00 ppm.

Procedure for Catalytic Hydrogenation of Benzophenone via 3. Potassium tri-*sec*-butylborohydride (62 μL of a 1.0 M solution) was added to a stirred suspension of **2** (10 mg, 0.015 mmol Ru) in 1 mL of C_6H_6, and the resulting solution was stirred at room temperature for 15 h. An aliquot (160 μL, 0.0024 mmol of Ru) of this standard solution was then added to benzophenone (1.31 g, 7.19 mmol) in 7 mL of 2-propanol or benzene. For reactions at atmospheric pressure, the resulting pink solution was degassed by three freeze−pump−thaw cycles and then placed under 1 atm of H_2 and stirred at 60 °C for 24 h. For reactions at higher pressures, the solution was loaded into a glass-lined autoclave, purged with H_2, pressurized to the designated pressure, and heated to the desired temperature for 18 or 24 h. Conversions, determined by ^{1}H NMR, are listed in Table 2 (reactions in duplicate, ±2%). Control experiments indicated 55% conversion on carrying out the above experiment in 2-propanol under an N_2 atmosphere.

Procedure for Catalytic Hydrogenation of Benzophenone via 5. (a) In Situ Preparation of 5 via 3. Potassium tri-*sec*-butylborohydride (62 μL of a 1.0 M solution) was added to a stirred suspension of **2** (10 mg, 0.015 mmol Ru) in 1 mL of C_6H_6, and the resulting solution was stirred at room temperature for 15 h. Benzophenone (27 mg, 0.15 mmol) was added to the yellow solution of **3**, causing a color change to dark red. After the mixture was stirred at room temperature for 5 h, complete conversion to **5** was confirmed by ^{31}P NMR. An aliquot (160 μL, 0.0024 mmol Ru) of this standard solution was then added to benzophenone (1.31 g, 7.19 mmol) in 7 mL of 2-propanol. The resulting pink solution was degassed by three freeze−pump−thaw cycles and then placed under 1 atm of H_2 and stirred at 60 °C for 24 h. Conversion determined by ^{1}H NMR: 96% Ph$_2$CHOH (reactions in duplicate, ±2%).

(b) In Situ Preparation of 5 via 2. To a stirred suspension of **2** (10 mg, 0.015 mmol Ru) in 1 mL of C_6H_6 was added KOCHPh$_2$ (7 mg, 0.031 mmol). The resulting dark red solution was stirred at room temperature for 1 h. Complete conversion to **5** was confirmed by ^{31}P NMR. An aliquot (160 μL, 0.0024 mmol of Ru) of this standard solution was then added to benzophenone (1.31 g, 7.19 mmol) in 7 mL of 2-propanol. The resulting pink solution was degassed by three freeze−pump−thaw cycles and then placed under 1 atm of H_2 and stirred at 60 °C for 24 h. Conversion determined by ^{1}H NMR: 95% Ph$_2$-CHOH (reactions in duplicate, ±2%).

(c) Large-Scale Reduction. Potassium tri-*sec*-butylborohydride (110 μL of a 1.0 M solution) was added to a stirred suspension of **2** (17.5 mg, 0.0275 mmol of Ru) in 3 mL of C_6H_6, and the resulting solution was stirred at room temperature for 15 h. Benzophenone (200 mg, 1.10 mmol) was added to the yellow solution, causing a color change to dark red. After the mixture was stirred at room temperature for 5 h, complete conversion to **5** was confirmed by ^{31}P NMR. The red catalyst solution was added to a solution of benzophenone (99.8 g) in 200 mL of 2-propanol, and the reaction mixture was refluxed under 1 atm of H_2. An aliquot withdrawn for ^{1}H NMR analysis showed 48% conversion within 1 h. A distillation apparatus was attached to the reaction vessel, and heating was continued. After a further 2 h of heating, conversions reached 90%.

Murai Coupling of Ethylene and Benzophenone. (a) Via 3. Potassium tri-*sec*-butylborohydride (62 μL of a 1.0 M solution) was added to a stirred suspension of **2** (10 mg, 0.015 mmol of Ru) in 1 mL of C_6H_6, and the resulting solution was stirred at room temperature for 15 h. An aliquot (300 μL, 0.0045 mmol of **3**) was withdrawn and diluted with 3 mL of C_6H_6. Benzophenone (13 mg, 0.071 mmol) was added, causing an immediate color change from yellow to pink. The solution was loaded into a glass-lined autoclave, purged with ethylene, pressurized to 260 psi, and stirred at 60 °C for 22 h. The monoinsertion product, 2-ethylbenzophenone,[39] was identified by ^{1}H NMR ($CDCl_3$): 58% conversion. Reactions at higher

temperatures (90 °C) produced mixtures of the mono- and disubstituted (2, 2′-diethylbenzophenone[39]) products.

(b) Via 5. Potassium tri-*sec*-butylborohydride (62 μL of 1.0 M solution) was added to a stirred suspension of **2** (10 mg, 0.015 mmol Ru) in 1 mL of C_6H_6, and the resulting solution was stirred at room temperature for 15 h. Benzophenone (40 mg, 0.22 mmol) was added, and stirring was continued at ambient temperature for 5 h, after which complete conversion to **5** was confirmed by ^{31}P NMR. An aliquot (300 μL, 0.0045 mmol of **5**) was withdrawn and diluted with 3 mL of C_6H_6. Benzophenone (12.6 mg, 0.069 mmol) was added. The solution was loaded into a glass-lined autoclave, purged with ethylene, pressurized to 260 psi, and stirred at 60 °C for 22 h. The monoinsertion product, 2-ethylbenzophenone,[39] was identified by ^{1}H NMR: 26% conversion.

Preparation of $RuCl_2(CO)(PCy_3)_2$. The literature route gives the complex in less than 35% yield.[40] In an alternative route, it was prepared by dissolving $RuHCl(CO)(PCy_3)_2$ (150 mg, 0.21 mmol) in 3 mL of $CHCl_3$. After 40 h at ambient temperature, the solution was concentrated to 0.5 mL and layered with acetone. The dark red, crystalline product was filtered off, washed with acetone (3 × 5 mL) and hexanes (3 × 5 mL), and then dried under vacuum. Yield: 112 mg (70%). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 35.2 (s). ^{1}H NMR (C_6D_6, δ): 2.73−1.02 (m, Cy). IR (Nujol; cm^{-1}): ν(CO) 1934.

Reaction of $RuCl_2(CO)(PCy_3)_2$ with $KOCHPh_2$. A solution of $RuCl_2(CO)(PCy_3)_2$ (10 mg, 0.0131 mmol) in 0.7 mL of C_6D_6 was stirred with $KOCHPh_2$ (6 mg, 0.027 mmol). After 1 h, $RuHCl(CO)(PCy_3)_2$[35] was evident as the major product by NMR (^{1}H, ^{31}P; >50% of total ^{31}P NMR integration), along with residual starting material, free PCy_3, and unidentified byproducts. Further decomposition is evident over a prolonged reaction time (20 h).

Reaction of $RuCl_2(CO)(PPh_3)_2(DMF)$ (1) with $KOCHPh_2$. A solution of $RuCl_2(CO)(PPh_3)_2(DMF)$ (**1**; 30 mg, 0.038 mmol) in 0.7 mL of C_6D_6 was stirred with $KOCHPh_2$ (34 mg, 0.15 mmol). After 20 h, ^{1}H NMR showed the characteristic[36] hydride peaks for $RuH_2(CO)(PPh_3)_3$. $^{31}P\{^1H\}$ NMR confirmed the identity of $RuH_2(CO)(PPh_3)_3$ as the main product (δ, C_6D_6): 55.6 (d, ^2J(PP) = 18 Hz), 43.41 (t, ^2J(PP) = 18 Hz). Several unidentified products and free PPh_3 were also observed.

Structural Determination of 3 and 5. 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 AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. 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.[41] No symmetry higher than triclinic was observed for **3** or **5**. Refinement in the centrosymmetric space group options yielded computationally stable and chemically reasonable results of refinement. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. The hydride ligands in **3** and **5** were located from the Fourier electron density difference maps and were refined with a riding model. A half-occupied toluene molecule was located cocrystallized at an inversion center in the asymmetric unit of **3**. Phenyl rings were refined as flat hexagonal rigid bodies. All other non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms not directly coordinated as hydride ligands were treated as idealized contributions. All scattering factors are contained in the SHEXTL 5.10 program library.[42] The crystallographic data for **3** and **5** are summarized in Table 4.

Table 4. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters for 3 and 5

	3	**5**
empirical formula	$C_{44.50}H_{87}BK_2OP_2Ru$	$C_{42}H_{62}O_2P_2Ru$
fw	890.16	761.93
cryst size, mm	0.10 × 0.08 × 0.05	0.10 × 0.10 × 0.03
temp, K	203(2)	203(2)
wavelength, Å	0.710 73	0.710 73
cryst syst, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a, Å	12.7045(19)	11.4140(11)
b, Å	14.274(2)	12.4646(12)
c, Å	16.288(2)	14.7309(14)
α, deg	70.154(3)	105.770(2)
β, deg	71.340(3)	95.353(2)
γ, deg	64.262(2)	105.010(2)
V, Å^3	2450.2(6)	1917.6(3)
Z	2	2
D_{calcd}, g cm^{-3}	1.207	1.320
μ(Mo Kα), cm^{-1}	5.85	5.26
F(000)	958	808
θ range collected, deg	1.36−20.81	1.46−28.67
no. of rflns	21969	14922
no. of indep rflns	5141	8631
no. of rflns obsd (>2σ(*I*))	5141	8631
R(int)	0.1034	0.0426
max, min transmissn	0.928 076, 0.760 371	0.928 074, 0.814 151
no. of data/restraints/params	5141/477/481	8631/0/428
goodness of fit on F^2	1.030	1.015
final R1, wR2 indices ($I > 2\sigma(I)$)[a]	0.0505, 0.1055	0.0439, 0.0714
final R1, wR2 indices (all data)	0.0923, 0.1184	0.0815, 0.0774
largest diff peak, hole, e Å^{-3}	0.510, −0.415	0.495, −0.588

[a] Definition of R indices: $R1 = \sum(F_o - F_c)/\sum(F_o)$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

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Supporting Information Available: X-ray crystallographic tables for **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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