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Inter- and Intramolecular Thermal Activation of sp^3 C−H Bonds with Ruthenium Bisallyl Complexes

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Complexes of type $[\{R_2P(CH_2)_nPR_2\}Ru(2\text{-Me-all})_2]$ (2-Me-all = 2-methylpropenyl; R = Cy, $n = 1-3$, **5a**−**c**; R = Me, $n = 2$, **6**; $R_2 = -(CH_2)_4-$, $n = 2$, **7**) have been synthesized from the reaction of the corresponding electron-rich diphosphines with $[(cod)Ru(2\text{-Me-all})_2]$ (**4**) at 50−70 °C. The new complexes were fully characterized by multinuclear NMR spectroscopy and mass spectroscopic techniques. Reacting **4** with $Cy_2P(CH_2)_nPCy_2$ containing hydrocarbon bridges with $n = 3$ (**1c**) and $n = 4$ (**1d**) at 95 and 50 °C, respectively, led to $[\kappa^2P,P'\text{-}\{(\eta^3\text{-}C_6H_8)CyP(CH_2)_nPCy_2\}Ru(\eta^3\text{-}C_8H_{13})]$ ($n = 3, 4$; **8c,d**) via *intramolecular* C−H bond activation and concomitant hydride transfer to cyclooctadiene. The molecular structure of **8c** was unambiguously assigned by multinuclear 1D and 2D NMR spectroscopy and confirmed by single-crystal X-ray diffraction. The new complexes were tested as homogeneous catalyst precursors in thermal *intermolecular* C−H activation processes. In dehydrogenation of cyclooctane (coa), an initial turnover frequency of 1.9 h^{-1} was observed using complex **5a** under refluxing conditions without the need of a hydrogen scavenger. A maximum total number of 5 catalytic turnovers was achieved after 48 h. Ligand degradation by dehydrogenation was detected under catalytic conditions, presumably initiated via intramolecular C−H activation as in species of type **8**. Attempts to utilize complexes **5** for C−H activation in $scCO_2$ as the reaction medium resulted in insertion of CO_2 into the Ru−allyl moiety, yielding catalytically inactive ruthenium carboxylates.

Introduction

Activation and functionalization of C−H bonds of simple hydrocarbons by organometallic compounds is an intensively studied area of considerable theoretical interest[1] and potential practical importance.[2] Late transition metal complexes have been addressed as promising materials to provide approaches to this ambitious goal.[3−5] Since the pioneering work of Shilov on homogeneously transition-metal-catalyzed alkane activation in 1969,[6] there has been steady progress especially in the development of efficient systems for dehydrogenation[7−11] and carbonylation/carboxylation processes.[12]

It has been shown that the unfavorable thermodynamics of alkane dehydrogenation can be overcome by photoirradiation,[7] by hydrogen transfer from alkane to sacrificial hydrogen acceptors,[7b,c,g,8−10] or—more recently—by thermal hydrogen evolution.[11] The dehydrogenation

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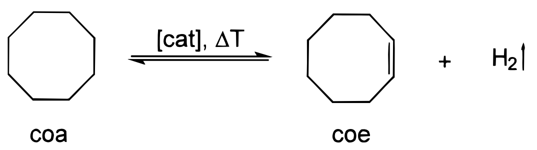
Scheme 1



of cyclooctane (coa) has been established as an ideal test reaction to probe the ability of an organometallic compound to achieve catalytic C−H bond activation.[7b,e] In a seminal study, Felkin and co-workers have shown that polyhydride complexes of ruthenium are active in thermal transfer−dehydrogenation of coa, but a large excess of the sacrificial hydrogen acceptor *tert*-butylethylene (tbe) was required for the formation of appreciable amounts of cyclooctene (coe) A maximum of 55 catalytic cycles was obtained after 7 days.[9a] Catalytic thermal dehydrogenation of coa under evolution of hydrogen (Scheme 1), however, is still rare and has been hitherto restricted to precious metal complexes based on iridium and rhodium.[11]

On the basis of previous experience with the activation of the H−H bond in the hydrogenation of CO_2,[13,14] we were interested in the potential of transition metal catalyst precursors containing thermolabile or chemically removable ligands and *cis*-bidentate chelating phosphines for C−H activation of simple alkanes. Our initial attempts focused on [(P_2)Rh(hfacac)] (P_2 = *cis*-bidentate phosphine, hfacac = κ^2O,O′-hexafluoroacetylacetonate), which were indeed found to enable thermal dehydrogenation of coa, but no catalytic turnover could be achieved.[11d] In search for thermally more robust, but structurally similar fragments of type [(P_2)M], we turned to Ru(II) as the coordination center and found that complexes [$(Cy_2P(CH_2)_nPCy_2)$Ru(2-Me-all)$_2$] (Cy = cyclohexyl, n = 1−3; **5a**−**c**) allow intra- and intermolecular thermal C−H activation, resulting in moderate catalytic turnover *in the absence of hydrogen acceptors*.[11d]

In the present contribution, we report details of the synthesis, characterization, and reactivity of **5a**−**c** and related bisallyl complexes of ruthenium. Complexes [κ^2P,P′-{(η^3-C_6H_8)CyP$(CH_2)_n$PCy$_2$}Ru(η^3-C_8H_{13})] (n = 3, 4; **8c,d**) resulting from intramolecular sp^3 C−H activation of ligand-bound cyclohexyl groups and containing a novel terdentate ligand system are described, and the first X-ray crystal structure analysis of such a complex is presented for **8c**. In addition, we provide a complete summary of the alkane activation results including a discussion of plausible deactivation mechanisms. Preliminary results on the use of $scCO_2$ as a reaction medium for catalytic C−H activation are also discussed briefly.

Results and Discussion

Synthesis and Structure of Complexes [{$R_2P(CH_2)_nPR_2$}Ru(2-Me-all)$_2$] 5a−c, 6, and 7. Bis(allyl)ruthenium complexes with phosphorus donor ligands have recently found numerous useful applications in organic synthesis and catalysis.[15,16] The new complexes **5a**−**c** are obtained from the reaction of [(cod)Ru(2-Me-all)$_2$] (cod = 1,5-cyclooctadiene; **4**) with 1 equiv of the appropriate bis(dicyclohexylphosphino)alkane **1a**−**c** at 50−70 °C in hexane under an inert atmosphere of argon (Scheme 2). The initially colorless solutions turn gradually to yellow-orange upon heating, and the course of reaction can be readily monitored by ^{31}P NMR spectroscopy on samples taken from septum-sealed vessels. Under careful temperature control, **1a**−**c** are converted with high selectivity to **5a**−**c** as the major phosphorus-containing species (vide infra).

Complexes **5a**−**c** precipitate from the reaction mixture upon cooling to room temperature and can be

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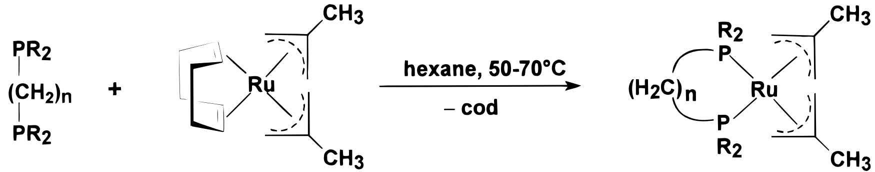
Scheme 2



1a; R = Cy; n = 1
1b; R = Cy; n = 2
1c; R = Cy; n = 3
2; R = Me; n = 2
3; R_2 = -$(CH_2)_4$-; n = 2

4

5a; 79%
5b; 76%
5c; 77%
6; 70%
7; 42%

isolated as off-white or pale yellow crystals in 75–80% total yield by filtration and further concentration of the mother liquors. All complexes are moderately air-stable in the solid state and can be stored over months without decomposition under argon atmosphere at room temperature. **5b** and **5c** are poorly to moderately soluble in hydrocarbons and aromatic solvents, whereas **5a** is almost insoluble in most organic solvents at ambient temperature. The solubility of **5a**–**c** is considerably higher in chlorinated solvents, but the complexes tend to decompose in these solutions upon standing.

The new complexes **5a**–**c** were fully characterized by NMR and IR spectroscopy as well as by mass spectroscopic (MS) and elemental analysis. The molecular ions are detectable in the MS spectra of all three complexes and similar fragmentation patterns are observed, indicating loss of the Me–allyl fragments, cyclohexyl groups, and PCy_2 units. Considerable H-shuffling during the analysis results in very broad line distributions around each characteristic mass, making exact assignments impossible. Most notably, however, significant amounts of benzene can be detected in the mass spectra which result from cyclohexyl dehydrogenation[4e,17–19] and subsequent $P-C_{aryl}$ cleavage;[20] this observation indicates already a high reactivity of **5a**–**c** for C–H bond activation.

Consistent with a C_2 symmetrical molecular structure, C_6D_6 solutions of complexes **5a**–**c** give rise to singlets in the expected region of the $^{31}P\{^1H\}$ NMR spectra. The downfield shift compared to the free ligands **1a**–**c** shows the typical dependence on the size of the P–Ru–P chelate ring.[21] The ^1H and ^{13}C resonances were fully assigned on basis of 2D homonuclear and heteronuclear correlation spectra and selective ^{31}P decoupling experiments for **5c** as the prototype of complexes $[(P_2)Ru(2\text{-Me-all})_2]$. The ^1H NMR spectrum is dominated by an area of overlapping multiplets between δ 1.0 and 1.9 arising from the cyclohexyl protons, whereby the definition of Cy1 and Cy2 is arbitrary (see Scheme 4 for numbering). The allylic proton resonances are shifted downfield, appearing as doublets of virtual triplets at δ 2.58 for the two *syn*-allylic protons in *cis*–*cis* position to phosphorus and as apparent doublets at δ 1.39 for the two *anti*-congeners. A doublet at δ 1.64 results from the resonances of the two *syn*-allylic protons in *cis*–*trans* position to phosphorus; the signal for the two *anti*-analogues is partly obscured at δ 1.20. The six methyl protons give rise to a characteristic sharp singlet at δ 2.21. The signals for the protons of the methylene units of the diphosphine backbone are located at δ 1.90 and δ 1.68 for the four protons at the two outer positions and at δ 1.84 for the two protons at the middle carbon.

Moving from downfield chemical shifts to higher field in the $^{13}C\{^1H\}$ spectrum, one first notes a singlet of the central allylic carbon at δ 93.0, which is absent in the DEPT spectra. The 2-methyl groups resonate as a singlet at δ 26.7, whereas the allylic methylene units give rise to virtual triplets at δ 39.7 in *cis,trans* position to phosphorus ($|^2J_{P-C} + {}^2J_{P'-C}| = 19.5$ Hz) and δ 33.8 in *cis,cis* position ($|^2J_{P-C} + {}^2J_{P'-C}| = 7.9$ Hz). The carbon atoms of the cyclohexyl rings directly attached to phosphorus ($Cy-C_1$) appear as the A parts of two degenerated AXX′ spin systems centered at δ 41.7 and δ 38.7, respectively. The remaining cyclohexylic carbons are grouped together as singlets at δ 31.3–30.5 for $Cy-C_2$ and at δ 27.3 and 27.1 for $Cy-C_4$ and as virtual triplets at δ 28.9–28.0 for $Cy-C_3$. The bridging methylene units exhibit the highest field ^{13}C resonances and give rise to a virtual triplet at δ 21.7 for the two carbons connected to phosphorus and a singlet at δ 20.4 for the middle carbon.

Slow crystallization (approximately 12–20 weeks) at −40 °C of a highly diluted mother liquor of complex **5b** in hexane led to single crystals that were suitable for single-crystal X-ray diffraction analysis. The molecular structure of **5b**, which was found to crystallize in the monoclinic crystal system, is shown together with selected structural parameters in Figure 1. The ruthenium central atom is coordinated to two phosphorus atoms and two η^3-allyl units. The coordination geometry can be considered distorted tetrahedral (P donor atoms + coordination centers of the η^3-allyl units) or distorted octahedral (P donor atoms + outer allylic carbon atoms).

The Ru–P bond distances of **5b** (Figure 1) fall within the range reported for the related complexes.[15b,22] Owing to the five-membered chelate ring, the P1–Ru–P2 angle differs significantly from an ideal tetrahedral angle, as observed also with the analogous (*S,S*)-CHIRAPHOS complex (85.0°)[15b] and in contrast to the

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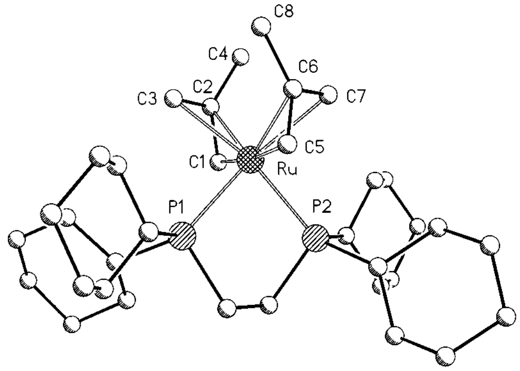

Figure 1. Molecular structure of [{$Cy_2P(CH_2)_2PCy_2$}Ru(2-Me-all)$_2$] (**5b**) as determined by single-crystal X-ray diffraction analysis. Heavy atoms are represented as spheres, and hydrogen atoms have been omitted for clarity. D(1) and D(2) denote the hypothetical coordinative center of the two η^3-allyl units. Selected bond distances (Å) and angles (deg): Ru−P(1), 2.335(1); Ru−P(2), 2.333(1); Ru−D(1) (C1,C2,C3), 1.952(1); Ru−D(2) (C5,C6,C7), 1.946(1); Ru−C(1), 2.219(4); Ru−C(2), 2.175(4); Ru−C(3), 2.248(5); Ru−C(5), 2.218(4); Ru−C(6), 2.174(4); Ru−C(7), 2.242(5); C(1)−C(2), 1.416(6); C(2)−C(3), 1.396(6); C(2)−C(4), 1.512(6); C(5)−C(6), 1.415(6); C(6)−C(7), 1.431(7); C(6)−C(8), 1.503(6); P(1)−Ru−P(2), 85.03(4); D(1)−Ru−D(2), 120.10(5); C(1)−C(2)−C(3), 118.6(4); C(5)−C(6)−C(7), 117.5(4).

monodentate phosphine coordinated complex [$(PPh_3)_2$Ru(all)$_2$] (109.9°).[22] The angle between the two allylic moieties is concomitantly widened to approximately 120° in the complexes with the chelating phosphines. The Ru−C distances follow the typical motive of short bonds to the outer carbons and longer bonds to the central carbon of the η^3-allyl ligand. The C−C bond lengths within the 2-Me−allyl fragment are in the expected range.

The related bisphosphine ruthenium bisallyl complexes **6**[15a] and **7** were prepared similarly from **4** and 1,2-bis(dimethylphosphino)ethane (**2**) or 1,2-bis(1-phospholano)ethane (**3**), respectively. In the case of ligand **3**, the course of reaction differed remarkably from those observed with other chelating phosphines, but complex **7** could be isolated as a mixture containing small amounts of **4** according to NMR spectroscopic analyses. This material was used without further purification for catalytic tests.

Synthesis and Structure of Complexes [κ^2P,P′-{(η^3-C_6H_8)CyP$(CH_2)_n$PCy$_2$}Ru(η^3-C_8H_{13})] 8c,d. ^{31}P NMR monitoring of the reaction of **4** with **1c** indicated formation of a second product at temperatures above 55 °C. This species was formed in a clean reaction on the expense of **5c**. The secondary product precipitated from hexane at high temperature and could be isolated in pure form after 10 h at 95 °C in 29% yield by filtering the hot reaction mixture. The new compound was unambiguously characterized as the η^3-cyclooctenyl complex **8c** (Scheme 3) by one- and two-dimensional multinuclear NMR spectroscopic techniques and X-ray crystal structure analysis. The most salient feature of its structure is a unique terdentate κ^2P,P′-(η^3-allyl) ligand arising from intramolecular cleavage of three adjacent C−H bonds in one of the cyclohexyl rings attached to the phosphorus donor of a chelating bisphosphane.[17,18,23] The intermolecular C−H-activation leading to a κ^2P,P′-(η^3-allyl) ligand becomes the predominant pathway even at lower temperatures if the butylene-bridged bisphosphane **1d** is reacted with the precursor **4** (Scheme 3). After 24 h at 50 °C, complex **8d** can be isolated in pure form by fractional crystallization in 32% yield. Monitoring the course of reaction by ^{31}P NMR spectroscopy showed no singlet of significant intensity in the region expected for complex **5d**.[24]

The tendency for intramolecular H-shuffling under conditions of mass spectroscopy is even more pronounced with compounds **8c** and **8d** compared to the related bisallyl complexes **5**−**7**. Only **8d** allows the detection of a weak molecular ion, and in both cases, there is evidence for the formation of degradation products containing more than one ruthenium center. Most significantly, cyclooctadiene and cyclooctatetraene can be identified as fragmentation products, and the base peak under typical EI conditions corresponds to the mass of benzene. In the case of **8c**, a peak at $m/e = 532$ (13%) suggests formation of the fragment [{$Cy_2P(CH_2)_3P(Cy)Ph$}Ru] in which one cyclohexyl group has been dehydrogenated completely to a phenyl substituent.

The $^{31}P\{^1H\}$ NMR spectrum of **8c** consists of two doublets at δ 72.9 and 27.7 ($^2J_{P-P'} = 34.3$ Hz), whereby the strongly downfield shifted resonance results from the P atom which is part of two chelate rings. Detailed assignment of the ^{1}H NMR resonances was possible with the aid of TOCSY and NOESY spectra (see Scheme 4 for numbering). The allylic proton resonances of the cyclohexenyl group are located at δ 5.56 for the central hydrogen and at δ 3.66 and δ 1.54 in *cis,cis* and *cis,trans* position to the P atoms, respectively. The allylic moiety of the cyclooctenyl ligand is characterized by a doublet of virtual triplets at δ 4.76 for the central proton and multiplets at δ 3.81 and δ 3.18 for the outer allylic hydrogen atoms. The highly unsymmetrical coordination mode of the tridentate ligand leads to six distinct signals for the diastereotopic protons at each of the methylene groups in the backbone of the phosphine unit.

In agreement with structure **8c**, the $^{13}C\{^1H\}$ spectrum shows 35 distinct signals with 25 methylene and 10 methine groups according to DEPT analysis. The allyl moiety in the cyclohexenyl ring is characterized by three apparent doublets at δ 75.9 ($J = 1.4$ Hz) for the central carbon and at δ 50.1 ($J = 3.5$ Hz) and δ 63.3 ($J = 31.1$ Hz) in *cis,cis* and *cis,trans* position to the P atoms, respectively. The phosphorus attached carbon atom of the cyclohexenyl ring exhibits a chemical shift similar to those of the other Cy groups, but its coupling constant $^1J_{C-H} = 132$ Hz differs significantly from typical values (122−124 Hz). The allylic carbon atoms of the cyclooctenyl ligand give rise to a singlet at δ 83.1 for the central position and slightly broadened resonances at δ 48.4 in *cis,cis* position and δ 47.8 (d, $J = 28$ Hz) in *cis,trans* position. The methylene groups in α and β position to the allyl moiety resonate between δ 36.1 and 28.1. The high-field shift of δ 25.9 for the γ-CH$_2$ group is typical for a boat conformation of the eight-membered ring, which is also supported by the large separation of the

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[23] For intramolecular activation of benzylic sp^3 C−H in Ru−allyl complexes see: Hirano, M.; Kurata, N.; Marumo, T.; Komiya, S. *Organometallics* **1998**, *17*, 501.

[24] A chemical shift in the range of δ 30 ± 10 is estimated for **5d** from the ^{31}P NMR data of **1a**−**c** together with the typical ring contribution of seven-membered chelates.

Scheme 3

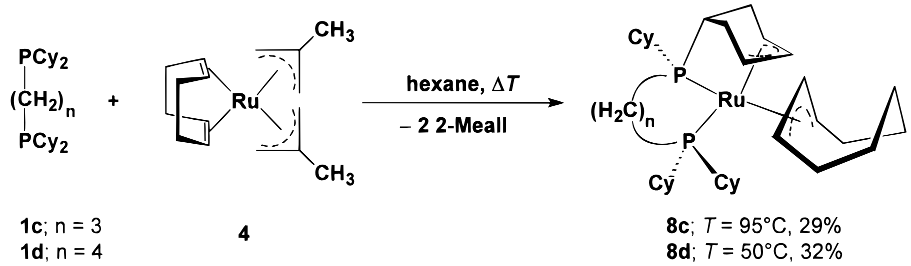

Table 1. Ruthenium-Mediated Thermal Dehydrogenation of Cyclooctane (coa)

complex	$c_{[\mathrm{Ru}]}$ [mmol l^{-1}]	t [h]	T^a [°C]	TON^b
4	12.9	48	170	0.5
5a	6.5	48	170	5.2
5a	7.0	1	120	0.6
5a	7.0	49	120	1.3
5b	4.6	52	170	3.2
5c	5.7	48	170	2.5
5c	6.3	168	170	4.0
6	6.1	48	170	1.4
7	12.6	48	170	0.6
8c	5.0	48	170	0.5
8d	5.4	50	170	1.3
9b	4.8	48	170	1.2
9c	4.6	48	170	5.5

[a] Bath temperature. [b] Total amount of coe per mole Ru-metal according to GC analysis.

attached *exo*- and *endo*-proton resonances (δ 1.51 and 2.57, respectively).[25]

The molecular structure of **8c**, as unambiguously derived from NMR measurements in solution, is also confirmed for the solid state by X-ray crystal structure analysis. Similar to **5b**, complex **8c** crystallizes in the monoclinic crystal system. The solubility properties of **8c** allowed only very small crystals to be grown, but the structure could still be solved with high accuracy and all hydrogen atoms were located and fully refined. As in **5c**, the ruthenium center in **8c** is surrounded by two allyl fragments and two P-donor atoms and the coordination geometry can be described in a similar manner. However, some significant distortions arise from the fact that one of the allyl ligands is part of a cyclohexenyl ring attached to a phosphorus donor atom of the chelating phosphine.

The angle at the middle carbon of the cyclohexenyl fragment, C(14)−C(15)−C(16), is considerably larger than the corresponding angles in the cylooctenyl ring or the open allyl ligands in complex **5c**. Furthermore, the cyclohexyl group has to bend toward the ruthenium atom to be able to act as an additional ligand. This is reflected in a small angle C(12)−P(1)−Ru below 100°, whereas the C−P−Ru angles for the nonactivated cyclohexyl phosphino groups are typically around 120°. Similarly, the angles between C(13)−C(12)−P(1) and C(17)−C(12)−P(1) are significantly smaller than the corresponding angles in the other cyclohexyl rings (113−115°). At the same time, the phosphorus atom connected to the activated cyclohexyl ring moves away from ruthenium, resulting in a Ru−P(1) distances that is ca. 0.48 Å longer than the $Cy_2P{-}Ru$ distances in **8c** and **5c**. The angle between the two coordination centers of the two η^3-allyl fragments in **8c** is 122°, i.e., slightly larger than the corresponding angle in **5c**, although the larger P−Ru−P angle in **8c** would be expected to lead to a smaller angle if the two allyl moieties were to adopt their positions without additional constraints.

Catalytic Thermal Intermolecular Activation of C−H bonds with Ruthenium Complexes 5−8. The unexpected isolation of compounds **8** and the results of the mass spectroscopic investigations of complexes **5** indicated a high activity of the fragment $[\{Cy_2P(CH_2)_n\text{-}PCy_2\}Ru]$ for thermal cleavage of nonactivated sp^3 C−H bonds. This encouraged us to investigate the potential of ruthenium complexes **5**−**8** for intermolecular processes of this type using the dehydrogenation of coa *in the absence of a hydrogen scavenger* as a test reaction (Scheme 1). In a standard procedure, carefully purified coa (≥99.993 GC purity) was heated to 170 ± 2 °C for 48 h in the presence of catalytic amounts of the appropriate ruthenium complex in a small Schlenk tube equipped with a reflux condenser. An inert atmosphere was ensured throughout the experiment by passing a gentle stream of argon over the reaction mixture on top of the reflux condenser. The refluxing conditions together with the gas stream were expected to remove any hydrogen and other gaseous products from the reaction vessel.[11] After cooling and removal of metal-containing species by passing the solution through a short pad of silica or by Kugelrohr distillation,[26] the liquid phase was quantitatively analyzed by gas chromatography using cyclohexane as an internal standard. Results are summarized in Table 1.

Complexes **5a**−**c** were indeed found to allow catalytic formation of coe by thermal dehydrogenation of coa, and the reaction was shown to occur at homogeneously dissolved metal species.[11d] The methylene-bridged complex **5a** exhibits the highest reaction rates with a turnover frequency in the initial state of up to 1.9 h^{-1}. The total number of catalytic turnovers (TON) after 48 h reaches a maximum of 5 using **5a** as the catalyst precursor. The length of the $-(CH_2)_n-$ spacer has only a small influence on the catalytic efficiency of **5a**−**c**, whereby the catalytic efficiency decreases somewhat in the order **5a** > **5b** > **5c**. With all three complexes, a considerable decrease of the rate of coe formation is observed within the first 5 h of reaction (Figure 3), indicating rapid catalyst deactivation by thermal degradation[11d] or product inhibition.[27]

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[25] (a) Lange, S.; Wittmann, K.; Gabor, B.; Mynott, R.; Leitner, W. *Tetrahedron: Asymmetry* **1998**, *9*, 475, and references therein. (b) For a related bisphosphine Ru−cyclooctenyl complex see: Wiles, J. A.; Lee, C. E.; McDonald, R.; Bergens, S. *Organometallics* **1996**, *15*, 3782.

[26] Both methodologies gave consistent results which were identical to results from direct injection of the mixture in control experiments.

[27] Addition of coe has been shown to retard the dehydrogenation of coa with Ir complexes containing pincer ligands.[11e]

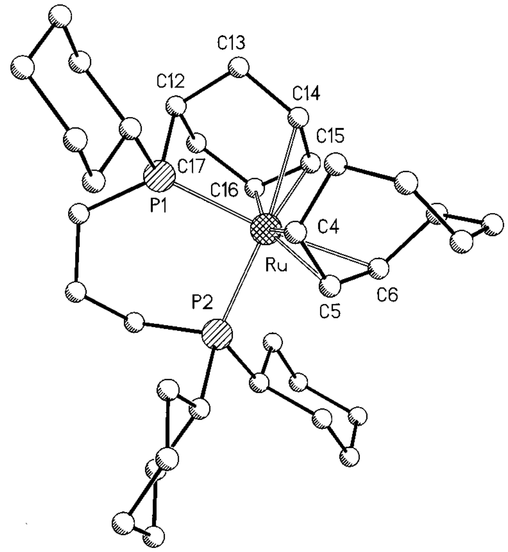

Figure 2. Molecular structure of [κ^2P,P′-{(η^3-C_6H_8)CyP(CH_2)$_3$-PCy_2}Ru(η^3-C_8H_{13})] (**8c**) as determined by single-crystal X-ray diffraction analysis. Heavy atoms are represented as spheres, and hydrogen atoms have been omitted for clarity. D(1) and D(2) denote the hypothetical coordinative center of the two η^3-allyl units of the cyclooctenyl and cyclohexenyl ligand, respectively. Selected bond distances (Å) and angles (deg): Ru−P(1), 2.817(1); Ru−P(2), 2.341-(1); Ru−D(1) (C4,C5,C6) 1.979(1); Ru−D(2) (C14,C15,C16) 1.981(1); Ru−C(4), 2.270(4); Ru−C(5), 2.151(3); Ru−C(6), 2.311(4); Ru−C(14), 2.261(4); Ru−C(15), 2.141(4); Ru−C(16), 2.305(5); P(1)−C(12), 1.842(4); C(12)−C(13), 1.530-(5); C(13)−C(14), 1.519(5); C(14)−C(15), 1.410(5); C(15)−C(16), 1.413(5); C(16)−C(17), 1.514(5); C(17)−C(12), 1.526(5); P(1)−Ru−P(2), 92.90(3); D(1)−Ru−D(2) 122.6(2); C(4)−C(5)−C(6), 122.7(4); C(14)−C(15)−C(16), 116.5(4).

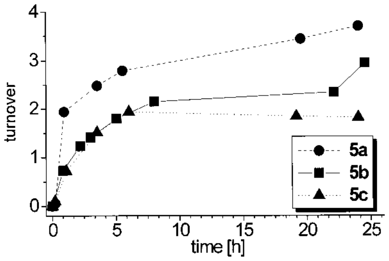

Figure 3. Time dependence of the thermal dehydrogenation of cyclooctane (coa) using complexes [{$Cy_2P(CH_2)_n$-PCy_2}Ru(2-Me-all)$_2$] (**5a**, $n = 1$; **5b**, $n = 2$; **5c**, $n = 3$) as catalysts at 170 °C bath temperature.

Complex **8c** is considerably less effective for coa dehydrogenation than its precursor **5c**. Furthermore, benzene could be detected by GC−MS in the final reaction mixtures after removal of all metal-containing species. These findings together with the results described above strongly suggest that ligand degradation via intramolecular C−H activation and subsequent P−aryl cleavage is one possible pathway for catalyst deactivation with complexes **5**. We have therefore extended our investigations to related bisallyl complexes with basic chelating phosphines containing substituents other than cyclohexyl at phosphorus. The isopropyl-substituted bisallyl complexes [{^{i}Pr$_2$P(CH_2)$_2$P^{i}Pr$_2$}Ru-(η^3-C_3H_5)$_2$] (**9b**) and [{^{i}Pr$_2$P(CH_2)$_3$P^{i}Pr$_2$}Ru(η^3-C_4H_7)$_2$] (**9c**)[15a] are also catalytically active, with efficiency for coe formation similar to their congeners of type **5**. The complexes **6** and **7** lacking a potentially cleavable C−H group in close proximity to the metal center give even lower yields of coe than **5b**. Therefore, other thermal deactivation pathways and/or product inhibition must also play an important role in limiting the catalytic efficiency of the ruthenium bisallyl complexes.

Despite their limitations, compounds **5**−**9** are the first examples of ruthenium complexes that have been shown to allow thermal catalytic dehydrogenation of coa in the absence of external hydrogen acceptors. It cannot be a priori excluded, however, that the two allylic ligands act as hydrogen scavengers accounting for up to three catalytic turnovers. We have therefore analyzed the liquid phase and the gas phase of typical experiments for C_4 components by GC−MS. After heating **5b** in cyclooctane to 170 °C for 48 h in a closed vessel, isobutane and isobutene could be detected, but no direct correlation was found between the amounts of coe and isobutane.

If *tert*-butylethylene (tbe) was added as a potential hydrogen acceptor,[9a] no enhancement of the formation of coe was observed under various conditions. When a coa/tbe solution of complex **5b** was heated to 120 °C in a closed system, only 0.8 catalytic turnover for coe formation was achieved, but almost 4 equiv of tbe were hydrogenated to *tert*-butylethane (tba). The excess hydrogen required for the reduction of tbe is most likely delivered by dehydrogenative degradation of the ligand's cyclohexyl groups. Highly efficient hydrogenation of tbe occurred without any coe formation when transfer−dehydrogenation was attempted with **5b** in the presence of H_2 under the conditions developed by Goldman.[9f] These results led to the conclusion that the reduction of tbe and the dehydrogenation of coa with complex **5b** are independent reactions, and transfer−dehydrogenation appears to play no significant role for the coe formation with complexes **5**.

Preliminary experiments were carried out to investigate the possible coupling of the intermolecular C−H activation at complexes **5** with subsequent reactions leading to functionalization other than dehydrogenation. In particular, we were interested in the potential of formal CO_2 insertion into the C−H bond of the alkane substrate.[13] Thus a mixture of a complex of type **5** and coa was pressurized with CO_2 in a window-equipped stainless steel autoclave and heated to temperatures that were sufficiently high to allow C−H cleavage in the absence of CO_2. The resulting temperatures and pressures were well above the critical data of CO_2 (T_c = 31 °C, p_c = 73.8 bar) and homogeneous slightly yellow solutions were observed in all cases. However, GC analysis revealed no evidence for the formation of cyclooctane carboxylic acid or any other functionalized derivative of coa under various conditions. Furthermore, dehydrogenation of coa and reduction of tbe were also suppressed completely in the presence of CO_2.

After venting the reaction mixtures, small amounts of a yellow solid could be isolated from the reactor. FT-IR spectroscopic analysis of this solid suggested the presence of a metal complex containing C=O units (two strong bands at 1652 and 1525 cm^{-1}), indicating the incorporation of CO_2 into the organometallic starting material **5c**. Therefore, NMR studies were carried out to investigate the reactivity of **5c** toward CO_2. ^{31}P{^{1}H}

NMR spectroscopic monitoring of the reaction of **5c** with $^{13}CO_2$ (5 bar) in C_6D_6 solution revealed the disappearance of the characteristic signals of the starting complex under formation of various new, partly broadened signals. After 36 h at 80−90 °C, the spectrum was dominated by two sets of signals each consisting of two sharp doublets (δ 105.5/32.7, $^2J_{PP'} = 40$ Hz; δ 93.3/30.1, $^2J_{PP'} = 40$ Hz) in a 3:1 ratio. Two strong new signals appeared also in the corresponding $^{13}C\{^1H\}$ NMR spectrum at δ 178.3 and 182.6, integrating in the same ratio. Although no exact structural assignment is possible on the basis of these data, they are most consistent with the formation of two isomeric carboxylate complexes formed by insertion of CO_2 into the ruthenium allyl moieties, similar to what has been observed for related nickel and palladium compounds by Wilke[28] and Jolly,[29] respectively. The lack of catalytic activity in the presence of compressed CO_2 arises therefore most likely from the reaction of the precursor molecules **5** with the heterocumulene, which prevents thermal removal of the allyl moieties to give the unsaturated species required for C−H bond cleavage.[30]

Conclusion

In conclusion, a series of new ruthenium bismethallyl complexes $[\{R_2P(CH_2)_nPR_2\}Ru(\eta^3\text{-}C_4H_7)_2]$ bearing chelating bidentate phosphines was synthesized, and it was shown that these complexes are effective precursors for thermal cleavage of nonactivated sp^3 C−H bonds. The reaction can proceed catalytically, as demonstrated for the dehydrogenation of cyclooctane to cyclooctene. Intramolecular C−H activation occurs very readily for complexes containing cyclohexyl-substituted phosphines with three or more methylene groups in the backbone of the chelating ligand. The activation of three adjacent C−H bonds of one cyclohexyl ring leads to unprecedented terdentate κ^2P,P′-(η^3-cyclohexyl) ligands. The formation of such species must be taken into account whenever highly coordinately unsaturated fragments of type $[\{Cy_2P(CH_2)_nPCy_2\}M]$ ($n = 3$, M = platinum group metal) are formed and may provide a possible low-energy pathway for catalyst deactivation in catalytic processes involving such intermediates.

Experimental Section

General Comments. All manipulations were carried out in an atmosphere of argon using standard Schlenk techniques in flame-dried glassware. Some of the experiments involve the use of closed glass reactors or compressed gases and require appropriate safety precautions.

Analytical Techniques. NMR spectra were recorded on a BRUKER AC 200, working at 200.1 MHz (^{1}H), 50.3 MHz (^{13}C), and 81.0 MHz (^{31}P), unless otherwise noted. Chemical shifts are given relative to TMS using the solvent resonances as internal standards for ^{1}H and ^{13}C, and to H_3PO_4 as external standard for ^{31}P. Gas chromatographic analyses for dehydrogenation experiments were performed with a temperature-programmed Hewlett-Packard 5890 Chem GC using a 60m RTX-1 capillary column with a flame ionization detector. The identities of alkanes and alkenes were further confirmed by comparison with authentic samples and GC/MS on a Finnigan MAT SSQ 7000 using a 60 m OV1 column. Mass spectroscopy of solid ruthenium phosphine complexes was performed on a Finnigan MAT 8200 via fractional evaporation/direct injection. Mass values are given for the ^{102}Ru isotope; $[Ru_1]^+$ designates characteristic fragments containing one Ru center, but cannot be assigned unambiguously owing to H-shuffling. Elemental analyses were carried out in the Mikroanalytische Laboratorien Dornis und Kolbe, Mülheim/Ruhr. Melting points of the ruthenium complexes were measured via differential scanning calorimetry (DSC) on a Mettler Toledo DSC 820.

High-Pressure Equipment. Some of the transfer−dehydrogenation experiments and the attempts for functionalization reactions with carbon dioxide were performed in two steel autoclaves of 27 or 225 mL volume, respectively. The reactors were equipped with two thick-walled glass windows, two valves, internal thermocouple, pressure gauge, and Teflon-coated stirring bar. NMR experiments with gaseous CO_2 were performed in a high-pressure 5 mm Wilmad NMR tube with a PTFE-needle valve.

Materials. Solvents for synthesis and crystallization were dried and distilled under argon prior to use. Hexane and pentane were distilled from sodium/potassium alloy, and benzene was distilled from CaH_2.[31] Traces of unsaturated hydrocarbons were removed from cyclooctane by the following procedure: the cycloalkane was treated with an ice-cooled mixture of concentrated sulfuric and nitric acids and washed several times with concentrated sulfuric acid until no further coloration developed in the acid layer. It was then washed alternately with water and aqueous Na_2CO_3 until neutral.[31] The organic phase was passed through a column of activated Al_2O_3, purified by preparative GC, and distilled from sodium. The purity of the cyclooctane obtained from this procedure was verified to be greater than 99.99% by analytical GC *prior* to use. *tert*-Butylethylene (tbe) was distilled and stored under argon over 3 Å molecular sieves.

The commercial starting materials [(cod)Ru(2-Me-all)$_2$] (**4**) and 1,1-bis(dicyclohexylphosphino)methane (**1a**) were purchased from Acros Organics and STREM Chemicals, respectively, and used as received. The ligands 1,2-bis(dicyclohexylphosphino)ethane (**1b**), 1,3-bis(dicyclohexylphosphino)propane (**1c**), and 1,4-bis(dicyclohexylphosphino)butane (**1d**) were synthesized according to literature procedures.[32] 1,2-Bis(dimethylphosphino)ethane (**2**) was synthesized by the method of Chatt and Hussain.[33] 1,2-Bis(1-phospholano)ethane (**3**) was obtained in 78% purity by addition of 2,2-dioxo-1,3,2-dioxathiepane to $H_2PCH_2CH_2PH_2$ following the procedure of Field.[34] The impurity consisted mainly of the monophospholane, which could not be separated effectively on the small scale. The complexes **9b** and **9c** were kindly provided by Prof. P. W. Jolly and co-workers.[16a]

The following numbering scheme is used for the assignment of characteristic NMR resonances in compounds **5a**−**c** and **8c**,**d**. Individual cyclohexyl carbons are denoted with superscript greek letters, if distinction was possible. Note that the numbering scheme (Scheme 4) is different from the one used in X-ray analyses depicted in Figures 1 and 2.

[(1a)Ru(2-Me-all)$_2$] (5a). **4** (311 mg, 0.974 mmol) and **1a** (398 mg, 1 equiv) were dissolved in hexane (40 mL) in a three-

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[28] Wilke, G. *Angew. Chem.* **1988**, *100*, 189; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185.

[29] Jolly, P. W. *Angew. Chem.* **1985**, *97*, 279; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 283.

[30] Supercritical CO_2 has been successfully used as an inert solvent for stoichiometric C−H activation with 16e cyclopentadienyl complexes: Jobling, M.; Howdle, S. M.; Healy, M. A.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1287.

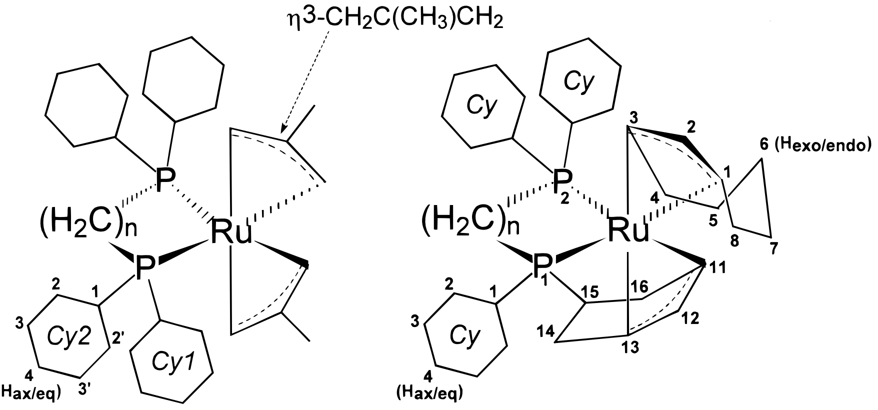
[31] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, 1988.

[32] (a) Issleib, K.; Müller, D. W. *Chem. Ber.* **1959**, *92*, 3175. (b) Dinjus, E.; Leitner, W. *Appl. Organomet. Chem.* **1995**, *9*, 43. (c) Priemer, H. Ph.D. Thesis, Ruhr-Universität Bochum, 1987.

[33] Burt, R. J.; Chatt, J.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1979**, *182*, 203.

[34] (a) Field, L. D.; Thomas, I. P. *Inorg. Chem.* **1996**, *35*, 2546. (b) For the solid-state structure of 2,2-dioxo-1,3,2-dioxathiepane see: Krüger, C.; Kessler, M.; Six, C.; Leitner, W. *Acta Crystallogr.* **1998**, *C54*, 389.

Scheme 4



5a; n = 1
5b; n = 2
5c; n = 3

8c; n = 3
8d; n = 4

necked flask equipped with argon inlet, reflux condenser, and a rubber septum. A solid started to precipitate after the colorless solution was heated to 50 °C (bath temperature) for 5 h. The resulting mixture was stirred at this temperature until the $^{31}P\{^1H\}$ NMR spectrum of a sample taken from the reaction mixture by syringe indicated quantitative consumption of **4** (13 h). After cooling to room temperature, the off-white precipitate was filtered off, washed with hexane (5 mL) and dried in vacuo to give almost colorless micorcrystals of **5a**. The bright yellow filtrate was concentrated in vacuo to 3 mL, affording a further crop of **5a**. Yield: 475 mg (0.766 mmol, 79%). Mp: 200 °C (dec 211 °C). Anal. Found: C, 63.77; H, 9.68; P, 10.20. Calcd for $C_{33}H_{60}P_2Ru$: C, 63.94; H, 9.76; P, 9.99. EI-MS (temperature of vaporization: 165 °C): $m/e = 620$ ($M^{\bullet+}$, 18), 505 ($[Ru_1]^+$, 100), 421 ($[Ru_1]^+$, 22), 339 ($[Ru_1]^+$, 10), 78 ($C_6H_6{}^+$, 13), 56 (C_4H_8+, 16), 41 ($C_3H_5{}^+$, 28). IR (KBr disk): 3044 m; 2991 m; 2926 s; 2846 s; 1718 w; 1443 s; 1366 m; 1348 m; 1331 m; 1292 w; 1263 m; 1224 w; 1196 m; 1171 m; 1117 m; 1068 s; 1022 s; 1001 s; 888 m; 848 s; 836 s; 763 s; 740 s; 674 m; 558 w; 525 m; 508 m; 466 m cm^{-1}. ^1H NMR (C_6D_6, 400.1 MHz, 300 K): δ 3.01 (m, 2H, η^3-CH_2C(CH_3)CH_2 syn, *cis,cis* to P and 2H, PCH_2), 2.36 (d, $^2J_{Hax-Heq} = 13.2$ Hz, 2H, Cy1−H_{2eq}), 2.19 (s, 6H, η^3-CH_2C(CH_3)CH_2), 1.98−0.85 (48H, cyclohexylic and remaining η^3-CH_2C(CH_3)CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz, 300 K): δ 93.6 (s, η^3-CH_2*C*(CH_3)CH_2), 43.4 (vt, $|^1J_{P-C} + {}^3J_{P'-C}| = 15.8$ Hz, Cy2−C_1), 37.9 (vt, $|^1J_{P-C} + {}^3J_{P'-C}| = 5.9$ Hz, Cy1−C_1), 34.9 (vt, $|^2J_{P-C} + {}^2J_{P'-C}| = 20.0$ Hz, η^3-$CH_2C(CH_3)$-*C*H_2 *cis,trans* to P), 34.2 (t, $^1J_{P-C} = 27.1$ Hz, P*C*H_2), 33.1 (partly obscured vt, η^3-*C*H_2C(CH_3)CH_2 *cis,cis* to P), 31.1 (s, Cy1−$C_{2'}$), 31.0 (s, Cy1−C_2), 30.3 (partly obscured vt, Cy2−C_2), 29.4 (vt, $|^2J_{P-C} + {}^4J_{P'-C}| = 5.7$ Hz, Cy2−$C_{2'}$), 28.4 (vt, $|^3J_{P-C} + {}^5J_{P'-C}| = 11.6$ Hz, Cy1−$C_{3'}$), 28.1 (m, Cy1−C_3), 28.0 (partly obscured vt, Cy2−$C_{3'}$), 27.8 (vt, $|^3J_{P-C} + {}^5J_{P'-C}| = 10.4$ Hz, Cy2−C_3), 27.0 (s, Cy1−C_4), 26.8 (s, η^3-CH_2C(*C*H_3)CH_2), 26.7 (s, Cy2−C_4). $^{31}P\{^1H\}$ NMR (C_6D_6, 81.0 MHz, 300 K): δ 6.8 (s).

[(1b)Ru(2-Me-all)$_2$] (**5b**). The synthesis was carried out as described for **5a** reacting **4** (582 mg, 1.82 mmol) and **1b** (774 mg, 1 equiv) in hexane (60 mL) at 60−70 °C (bath temperature) for 22 h. The solution was evaporated to dryness, and the resulting pale yellow solid was washed with 2 × 5 mL pentane and dried in vacuo. Yield: 878 mg (1.39 mmol, 76%). Mp: 153 °C (dec 216 °C). Anal. Found: C, 64.43; H, 9.41; P, 9.93. Calcd for $C_{34}H_{62}P_2Ru$: C, 64.42; H, 9.86; P, 9.77.

EI-MS (temperature of vaporization: 137 °C): $m/e = 634$ ($M^{\bullet+}$, 10%), 519 ($[Ru_1]^+$, 100), 435 ($[Ru_1]^+$, 14), 353 ($[Ru_1]^+$, 8), 78 ($C_6H_6{}^+$, 4), 56 ($C_4H_8{}^+$, 55), 41 ($C_3H_5{}^+$, 73). IR (KBr disk): 3069 m; 3035 m; 2926 s; 2845 s; 1444 s; 1420 m; 1341 w; 1265 w; 1173 m; 1120 m; 1068 m; 1047 w; 1020 s; 1000 m; 911 w; 888 m; 871 m; 839 m; 816 m; 783 w; 729 m; 707 w; 682 w; 653 w; 569 w; 554 m; 523 s cm^{-1}. ^1H NMR (C_6D_6, 300.1 MHz, 302 K): δ 2.52 (d, $^2J_{Hax-Heq} = 8.5$ Hz, 2H, Cy1−$H_{2'eq}$), 2.25 (s, 6H, η^3-CH_2C(CH_3)CH_2), 2.21 (partly obscured d, 2H, η^3-CH_2C(CH_3)-CH_2 syn, *cis,cis* to P), 2.15 (d, $|^2J_{P-H} + {}^3J_{P'-H}| = 8.5$ Hz, 2H, PCH_2), 2.06 (2H, Cy1−$H_{3'eq}$), 2.04 (2H, η^3-$CH_2C(CH_3)$CH_2 syn, *cis,trans* to P), 2.03 (2H, Cy1−H_{3eq}), 2.01 (2H, Cy1−H_1), 1.87 (2H, Cy2−H_{2eq}), 1.83 (2H, Cy2−H_1), 1.76 (2H, Cy1−H_{2eq}), 1.74 (2H, Cy1−H_{3ax}), 1.63 (2H, Cy1−H_{4eq} and 2H, Cy2−$H_{2'eq}$), 1.57 (2H, Cy2−H_{3eq} and 2H, Cy2−$H_{3'eq}$), 1.51 (2H, η^3-CH_2C(CH_3)-CH_2 anti, *cis,cis* to P), 1.47 (2H, Cy1−$H_{2'ax}$ and 2H, Cy2−H_{4eq} and 2H, Cy2−H_{2ax}), 1.35 (2H, Cy2−$H_{2'ax}$), 1.30 (2H, Cy1−$H_{3'ax}$ and 2H, η^3-$CH_2C(CH_3)$CH_2 anti, *cis,trans* to P), 1.21 (2H, Cy1−H_{2ax}), 1.18 (2H, Cy1−H_{4ax}), 1.09 (2H, PCH_2), 1.05 (2H, Cy2−H_{4ax}), 1.02 (2H, Cy2−H_{3ax} and 2H, Cy2−$H_{3'ax}$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.5 MHz, 302 K): δ 93.4 (s, η^3-CH_2*C*(CH_3)CH_2), 46.9 (vt, $|^1J_{P-C} + {}^3J_{P'-C}| = 26.9$ Hz, $^1J_{C-H} = 121 \pm 2$ Hz, Cy2−C_1), 38.0 (partly obscured vt, $^1J_{C-H} = 124 \pm 2$ Hz, Cy1−C_1), 35.3 (m, $|^2J_{P-C} + {}^2J_{P'-C}| = 20.3$ Hz, $^1J_{C-H} \approx 150$ Hz, η^3-$CH_2C(CH_3)$-*C*H_2 *cis,trans* to P), 32.2 (vt, $|^2J_{P-C} + {}^2J_{P'-C}| = 7.1$ Hz, $^1J_{C-H} = 153 \pm 3$ Hz, η^3-*C*H_2C(CH_3)CH_2 *cis,cis* to P), 31.7 (vt, $|^2J_{P-C} + {}^4J_{P'-C}| = 4.1$ Hz, $^1J_{C-H} \approx 128$ Hz, Cy1−$C_{2'}$), 31.1 (s, $^1J_{C-H} \approx 130$ Hz, Cy1−C_2), 30.4 (s, Cy2−$C_{2'}$), 30.2 (vt, $|^2J_{P-C} + {}^4J_{P'-C}| = 4.1$ Hz, Cy2−C_2), 28.8 (vt, $|^3J_{P-C} + {}^5J_{P'-C}| = 14.2$ Hz, $^1J_{C-H} \approx 124$ Hz, Cy1−$C_{3'}$), 28.7 (vt, $|^1J_{P-C} + {}^2J_{P'-C}| = 40.7$ Hz, P*C*H_2), 28.3 (vt, $|^3J_{P-C} + {}^5J_{P'-C}| = 10.3$ Hz, Cy1−C_3), 28.2 (partly obscured vt, $^1J_{C-H} \approx 128$ Hz, Cy2−$C_{3'}$), 28.0 (vt, $|^3J_{P-C} + {}^5J_{P'-C}| = 7.1$ Hz, Cy2−C_3), 27.2 (s, $^1J_{C-H} = 127 \pm 2$ Hz, Cy1−C_4), 26.8 (s, $^1J_{C-H} = 128 \pm 3$ Hz, η^3-CH_2C(*C*H_3)CH_2), 26.7 (s, $^1J_{C-H} = 126 \pm 3$ Hz, Cy2−C4). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz, 302 K): δ 63.8 (s).

[(1c)Ru(2-Me-all)$_2$] (**5c**). The synthesis was carried out as described for **5a** reacting **4** (850 mg, 2.66 mmol) with **1c** (1.16 g, 1 equiv) in 50 mL of hexane at 50−55 °C (bath temperature) for 5 h. After cooling, $^{31}P\{^1H\}$ NMR control of a sample taken from the orange homogeneous solution indicated quantitative conversion of the free phosphine with 92% formation of **5c**, 4% of **8c,** and 4% of other phosphorus-containing impurities. The solution was evaporated to dryness and the resulting light-orange solid washed with 3 × 5 mL of pentane, giving analytically pure **5c** as a pale yellow powder after drying in vacuo. Yield: 1.33 g (2.05 mmol, 77%). Mp: 151 °C (dec 165 °C). Anal. Found: C, 64.74; H, 9.88; P, 9.45. Calcd for $C_{35}H_{64}P_2$-Ru: C, 64.88; H, 9.96; P, 9.56. EI-MS (temperature of vaporization: 130 °C): $m/e = 648$ ($M^{\bullet+}$, 0.3%), 532 ($[Ru_1]^+$, 8), 450 ($[Ru_1]^+$, 3), 365 ($[Ru_1]^+$, 2), 78 ($C_6H_6{}^+$, 2), 56 ($C_4H_8{}^+$, 54), 41 ($C_3H_5{}^+$, 100). IR (KBr disk): 3071 m; 3035 m; 2920 s; 2847 s; 1443 s; 1421 m; 1344 w; 1263 w; 1168 m; 1112 m; 1022 s; 1001 m; 967 m; 890 m; 850 m; 829 s; 782 m; 726 m; 638 m; 500 m cm^{-1}. ^1H NMR (C_6D_6, 400.1 MHz, 300 K): δ 2.58 (dvt,

$^2J_{\mathrm{Hsyn-Hanti}} = 2.3$ Hz, $|^3J_{\mathrm{P-H}} + {}^3J_{\mathrm{P'-H}}| \approx 5.0$ Hz, 2H, η^3-CH_2C(CH$_3$)CH$_2$ syn, *cis,cis* to P), 2.39 (d, $^2J_{\mathrm{Hax-Heq}} = 10.4$ Hz, 2H, Cy1−H$_{2\mathrm{eq}}$), 2.21 (s, 6H, η^3-CH$_2$C(CH_3)CH$_2$), 2.14 (d, $^2J_{\mathrm{Hax-Heq}} = 11.6$ Hz, 2H, Cy1−H$_{2'\mathrm{eq}}$), 1.91 (2H, Cy2−H$_1$), 1.90 (2H, PCH_2), 1.84 (2H, PCH$_2$CH_2), 1.83 (2H, Cy1−H$_{3\mathrm{eq}}$ and 2H, Cy1−H$_{3'\mathrm{eq}}$), 1.78 (2H, Cy2−H$_{2'\mathrm{eq}}$), 1.76 (2H, Cy1−H$_1$), 1.74 (2H, Cy2−H$_{2\mathrm{eq}}$), 1.69 (2H, Cy1−H$_{4\mathrm{eq}}$), 1.68 (2H, PCH_2 and 2H, Cy2−H$_{3'\mathrm{eq}}$), 1.64 (d, $|^3J_{\mathrm{P-H}} + {}^3J_{\mathrm{P'-H}}| \approx 9.2$ Hz, 2H, η^3-CH$_2$C(CH$_3$)CH_2 syn, *cis,trans* to P), 1.62 (2H, Cy2−H$_{3\mathrm{eq}}$), 1.58 (2H, Cy2−H$_{4\mathrm{eq}}$), 1.39 (d, $|^3J_{\mathrm{P-H}} + {}^3J_{\mathrm{P'-H}}| \approx 14.0$ Hz, 2H, η^3-CH_2C(CH$_3$)CH$_2$ anti, *cis,cis* to P), 1.34 (2H, Cy1−H$_{2\mathrm{ax}}$ and 2H, Cy2−H$_{2'\mathrm{ax}}$), 1.32 (2H, Cy1−H$_{3\mathrm{ax}}$), 1.30 (2H, Cy1−H$_{2'\mathrm{ax}}$), 1.21 (2H, Cy2−H$_{3\mathrm{ax}}$), 1.20 (br, 2H, η^3-CH$_2$C(CH$_3$)CH_2 anti, *cis,trans* to P and 2H, Cy2−H$_{2\mathrm{ax}}$ and 2H, Cy1−H$_{3'\mathrm{ax}}$ and 2H, Cy1−H$_{4\mathrm{ax}}$), 1.14 (2H, Cy2−H$_{3'\mathrm{ax}}$), 1.07 (2H, Cy2−H$_{4\mathrm{ax}}$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz, 300 K): δ 93.0 (s, η^3-CH$_2$C(CH$_3$)CH$_2$), 41.7 (vt, $|^1J_{\mathrm{P-C}} + {}^3J_{\mathrm{P'-C}}| = 20.0$ Hz, $^1J_{\mathrm{C-H}} = 118 \pm 2$ Hz, Cy2−C$_1$), 39.7 (vt, $|^2J_{\mathrm{P-C}} + {}^2J_{\mathrm{P'-C}}| = 19.5$ Hz, η^3-CH$_2$C(CH$_3$)CH$_2$ *cis,trans* to P), 38.7 (vt, $|^1J_{\mathrm{P-C}} + {}^3J_{\mathrm{P'-C}}| = 6.2$ Hz, $^1J_{\mathrm{C-H}} = 122 \pm 2$ Hz, Cy1−C$_1$), 33.8 (vt, $|^2J_{\mathrm{P-C}} + {}^2J_{\mathrm{P'-C}}| = 7.9$ Hz, $^1J_{\mathrm{C-H}} = 150 \pm 2$ Hz, η^3-CH$_2$C(CH$_3$)CH$_2$ *cis,cis* to P), 31.3 (s, $^1J_{\mathrm{C-H}} = 127 \pm 2$ Hz, Cy1−C$_{2'}$), 31.0 (s, Cy1−C$_2$), 30.9 (s, Cy2−C$_2$), 30.5 (partly obscured vt, $^1J_{\mathrm{C-H}} = 125 \pm 2$ Hz, Cy2−C$_{2'}$), 28.9 (vt, $|^3J_{\mathrm{P-C}} + {}^5J_{\mathrm{P'-C}}| = 9.0$ Hz, Cy1−C$_{3'}$), 28.7 (vt, $|^3J_{\mathrm{P-C}} + {}^5J_{\mathrm{P'-C}}| = 9.4$ Hz, Cy1−C$_3$), 28.6 (vt, $|^3J_{\mathrm{P-C}} + {}^5J_{\mathrm{P'-C}}| = 5.4$ Hz, Cy2−C$_{3'}$), 28.0 (vt, $|^3J_{\mathrm{P-C}} + {}^5J_{\mathrm{P'-C}}| = 9.2$ Hz, $^1J_{\mathrm{C-H}} = 127 \pm 2$ Hz, Cy2−C$_3$), 27.3 (s, Cy1−C$_4$), 27.1 (s, Cy2−C$_4$), 26.7 (s, η^3-CH$_2$C(CH$_3$)CH$_2$), 21.7 (vt, $|^1J_{\mathrm{P-C}} + {}^3J_{\mathrm{P'-C}}| = 23.8$ Hz, $^1J_{\mathrm{C-H}} \approx 122 \pm 2$ Hz, PCH$_2$), 20.4 (s, $^1J_{\mathrm{C-H}} = 129 \pm 2$ Hz, PCH$_2$CH$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162.0 MHz, 300 K): δ 22.1 (s).

[(2)Ru(2-Me-all)$_2$] (**6**). The synthesis was carried out as described for **5a** reacting **4** (1.19 g, 3.71 mmol) with **2** (648 mg, 93% pure, approximately 1 equiv) in 45 mL of hexane at 70 °C (bath temperature). After 15 min the color of the solution changed from greenish to yellow. The ^{31}P{^{1}H} NMR of a sample taken after 13 h indicated almost quantitative conversion of **2**. The reaction was cooled to room temperature after 15 h and the yellow solution filtered from a small amount of a gray precipitate. The filtrate was evaporated to dryness and the resulting pale yellow solid dried in vacuo. Yield: 942 mg (2.61 mmol, 70%). Anal. Found: C, 46.47; H, 8.57; P, 17.16. Calcd for C$_{14}$H$_{30}$P$_2$Ru: C, 46.53; H, 8.37; P, 17.14. EI-MS (temperature of vaporization: 30 °C): *m/e* = 362 (M$^{\bullet+}$, 65), 345 ([Ru$_1$]$^+$, 16**)**, 307 ([Ru$_1$]$^+$, 87), 251 ([Ru$_1$]$^+$, 100), 57 (C$_4$H$_9^+$, 4), 41 (C$_3$H$_5^+$, 4). IR (KBr disk): 3033 m; 3011 m; 2963 s; 2897 s; 1414 s; 1365 m; 1272 m; 1023 m; 930 s; 883 s; 831 s; 791 m; 716 m; 692 m; 644 m; 572 w cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 200.1 MHz, 300 K): δ 2.23 (s, 6H, η^3-CH$_2$C(CH_3)CH$_2$), 2.13 (m, $^2J_{\mathrm{Hsyn-Hanti}} = 2.3$ Hz, $|^3J_{\mathrm{P-H}} + {}^3J_{\mathrm{P'-H}}| \approx 5.0$ Hz, 2H, η^3-CH_2C(CH$_3$)CH$_2$ syn, *cis,cis* to P), 1.50 (partly obscured vt, 2H, η^3-CH$_2$C(CH$_3$)CH_2 syn, *cis,trans* to P), 1.27 (d, $^2J_{\mathrm{P-H}} = 8.1$ Hz, 6H, PCH_3), 1.17 (dd, $^2J_{\mathrm{P-H}} = 13.5$ Hz/$^3J_{\mathrm{P-H}} = 1.5$ Hz, 4H, PCH_2), 1.07 (vt, $|^3J_{\mathrm{P-H}} + {}^3J_{\mathrm{P'-H}}| \approx 12.2$ Hz, 2H, η^3-CH_2C(CH$_3$)CH$_2$ anti, *cis,cis* to P), 0.80 (vt, $|^3J_{\mathrm{P-H}} + {}^3J_{\mathrm{P'-H}}| \approx 15.4$ Hz, 2H, η^3-CH$_2$C(CH$_3$)CH_2 anti, *cis,trans* to P), 0.56 (d, $^2J_{\mathrm{P-H}} = 6.7$ Hz, 6H, PCH_3). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz, 300 K): δ 94.3 (s, η^3-CH$_2$C(CH$_3$)CH$_2$), 39.9 (vt, $|^2J_{\mathrm{P-C}} + {}^2J_{\mathrm{P'-C}}| = 20.0$ Hz, η^3-CH$_2$C(CH$_3$)CH$_2$ *cis,trans* to P), 34.2 (vt, $|^2J_{\mathrm{P-C}} + {}^2J_{\mathrm{P'-C}}| = 7.7$ Hz, η^3-CH$_2$C(CH$_3$)CH$_2$ *cis,cis* to P), 31.3 (vt, $|^1J_{\mathrm{P-C}} + {}^3J_{\mathrm{P'-C}}| = 46.2$ Hz, PCH$_3$), 27.0 (s, η^3-CH$_2$C(CH$_3$)CH$_2$), 22.5 (vt, $|^1J_{\mathrm{P-C}} + {}^2J_{\mathrm{P'-C}}| = 24.5$ Hz, PCH$_2$), 10.1 (vt, $|^1J_{\mathrm{P-C}} + {}^3J_{\mathrm{P'-C}}| = 17.4$ Hz, PCH$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 81.0 MHz, 300 K): δ 48.8 (s).

[(3)Ru(2-Me-all)$_2$] (**7**). The synthesis was carried out as described for **5a** reacting **4** (881 mg, 2.76 mmol) and **3** (522 mg, 78% purity, approximately 1 equiv) at 60−70 °C (bath temperature) in hexane (15 mL) for 4 h. Upon heating, a solid precipitated rapidly and the reaction mixture darkened quickly from yellow to dark brown. The brown solid was filtered off and found to contain a complex mixture of compounds by ^{31}P{^{1}H} NMR analysis. Evaporation of the filtered solution gave a dark brown viscous material, which solidified to an amorphous solid by cooling to −78 °C. This material consisted of the desired new complex **7** as the only phosphorus-containing compound, together with small amounts of unreacted **4**. Yield: 482 mg (1.17 mmol, 42%). EI-MS (temperature of vaporization: 90 °C): *m/e* = 414 (M$^{\bullet+}$, 51%), 410 ([Ru$_1$]$^+$, 100), 357 ([Ru$_1$]$^+$, 45), 301 ([Ru$_1$]$^+$, 71), 268 ([Ru$_1$]$^+$, 56), 241 ([Ru$_1$]$^+$, 24), 55 (C$_4$H$_7^+$, 13), 41 (C$_3$H$_5^+$, 23). IR (neat): 3018 s; 2934 s; 2858 s; 2823 m; 2716 w; 1446 s; 1410 s; 1366 s; 1347 m; 1176 m; 1109 s; 1022 s; 1001 m; 949 m; 884 s; 864 s; 692 s; 646 s; 579 m; 566 m; 518 s cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 200.1 MHz, 300 K): δ 2.87 (partly obscured dvt, $|^3J_{\mathrm{P-H}} + {}^3J_{\mathrm{P'-H}}| \approx 12.0$ Hz, 2H, η^3-CH_2C(CH$_3$)CH$_2$ syn, *cis,cis* to P), 2.67 (s, 6H, η^3-CH$_2$C(CH_3)CH$_2$), 2.0−0.8 (m, 26H, heterocyclic, ligand backbone and allylic protons). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 50.3 MHz, 300 K): δ 93.9 (s, η^3-CH$_2$C(CH$_3$)CH$_2$), 40.8 (vt, $|^2J_{\mathrm{P-C}} + {}^2J_{\mathrm{P'-C}}| = 20.1$ Hz, η^3-CH$_2$C(CH$_3$)CH$_2$ *cis,trans* to P), 34.1 (vt, $|^1J_{\mathrm{P-C}} + {}^3J_{\mathrm{P'-C}}| = 25.9$ Hz, PCH$_2$ cycl.), 33.8 (vt, $|^2J_{\mathrm{P-C}} + {}^2J_{\mathrm{P'-C}}| = 7.7$ Hz, η^3-CH$_2$C(CH$_3$)CH$_2$ *cis,cis* to P), 31.6 (vt, $|^1J_{\mathrm{P-C}} + {}^3J_{\mathrm{P'-C}}| = 42.0$ Hz, PCH$_2$ cycl.), 27.9 (partly obscured vt, PCH$_2$CH$_2$ cycl.), 27.4 (s, PCH$_2$CH$_2$ cycl.), 27.0 (s, η^3-CH$_2$C(CH$_3$)CH$_2$), 19.8 (vt, $|^1J_{\mathrm{P-C}} + {}^2J_{\mathrm{P'-C}}| = 14.8$ Hz, PCH$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 81.0 MHz, 300 K): δ 83.0 (s).

[κ^2P,P′-{(η^3-C$_6$H$_8$)CyP(CH$_2$)$_3$PCy$_2$}Ru(η^3-C$_8$H$_{13}$)] (**8c**). **4** (1.03 g, 3.23 mmol) and **1c** (1.40 g, 1 equiv) were dissolved in hexane (60 mL), and the almost colorless solution was heated to 95 °C (bath temperature) for 10 h. After cooling to room temperature, a pale orange solid precipitated from the red-brown homogeneous solution. The reaction mixture was concentrated in vacuo to 10 mL, and the precipitate isolated by filtration. The solid was washed with cold hexane (2 × 10 mL) and dried in vacuo to give analytically pure **8c**. Yield: 599 mg (0.93 mmol, 29%). Mp: 199 °C (dec 206 °C). Anal. Found: C, 64.91; H, 9.88; P, 9.59. Calcd for C$_{35}$H$_{60}$P$_2$Ru: C, 65.29; H, 9.39; P, 9.62. EI-MS (temperature of vaporization: 195 °C): *m/e* = 638 ([Ru$_1$]$^+$, 21), 555 ([Ru$_1$]$^+$, 12), 532 ([Ru$_1$]$^+$, 13), 450 ([Ru$_1$]$^+$, 14), 368 ([Ru$_1$]$^+$, 9), 108 (C$_8$H$_{12}^+$, 18), 78 (C$_6$H$_6^+$, 100). IR (KBr disk): 3016 m; 2919 s; 2845 s; 1442 s; 1415 m; 1336 w; 1266 w; 1169 m; 1150 m; 1117 m; 1041 m; 1003 m; 886 m; 850 m; 829 s; 768 m; 724 m; 639 m; 513 m cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 600.2 MHz, 303 K): δ 5.56 (vt, $^3J_{\mathrm{H11-H}} \approx 6.4$ Hz, $^3J_{\mathrm{H13-H}} \approx 6.4$ Hz, 1H, H$_{12}$), 4.76 (dvt, $^2J_{\mathrm{P2-H}} = 13.4$ Hz, $^3J_{\mathrm{H1-H}} \approx 7.6$ Hz, $^3J_{\mathrm{H3-H}} \approx 7.6$ Hz, 1H, H$_2$), 3.81 (m, $^3J_{\mathrm{H2-H}} \approx 8.3$ Hz, $^3J_{\mathrm{H4-H}} \approx 8.3$ Hz, 1H, H$_3$, *cis,cis* to P), 3.66 (m, 1H, H$_{13}$, *cis,cis* to P), 3.18 (m, $^3J_{\mathrm{H2-H}} \approx 8.2$ Hz, $^3J_{\mathrm{H8-H}} \approx 8.9$ Hz, 1H, H$_1$, *cis,trans* to P), 2.61/1.14 (m/−, $|^3J_{\mathrm{H-H}}| \approx 13.5$ Hz/−, 1H each, Cy−H$_2$ adjacent to cyclohexenylic moiety), 2.57 (m, 1H, H$_6$ *endo*), 2.34 (br, 1H, H$_4$), 2.02 (m, 1H, H$_8$), 1.97 (1H, H$_{15}$), 1.95 (dd, $^3J_{\mathrm{P1-H}} = 38.4$ Hz, $|^3J_{\mathrm{H-H}}| = 13.3$ Hz, 1H, H$_{14}$), 1.91 (1H, H$_4$), 1.87/1.22 (1H each, Cy−H$_2^{\beta}$), 1.87 (1H, Cy−H$_1^{\beta}$), 1.86/1.34 (1H each, Cy−H$_2^{\alpha}$), 1.85/1.39 (1H each, Cy−H$_3^{\beta}$), 1.81 (1H, H$_7$), 1.75 (1H, H$_5$ and 1H, PCH$_2$CH_2), 1.74/1.16 (1H each, Cy−H$_3^{\alpha}$), 1.72 (1H, Cy−H$_1^{\gamma}$), 1.72/1.16 (2H each, Cy−H$_2^{\delta,\epsilon}$), 1.70/1.16 (1H each, Cy−H$_3^{\delta}$), 1.69 (1H, H$_7$), 1.69/1.04 (1H each, Cy−H$_3^{\epsilon}$), 1.68 (1H, H$_{16}$), 1.67/1.08 (1H each, Cy−H$_3^{\gamma}$), 1.67/1.18 (1H each, Cy−H$_3^{\delta}$), 1.66/1.13 (1H each, Cy−H$_4^{\alpha}$), 1.64/1.15 (1H each, Cy−H$_2^{\gamma}$), 1.64 (1H, PCH$_2$CH_2), 1.60 (1H, H$_5$), 1.60/1.17 (1H each, Cy−H$_4^{\beta}$), 1.58/1.07 (1H each, Cy−H$_4^{\gamma}$), 1.54 (1H, H$_{11}$, *cis,trans* to P and 1H, P1CH_2), 1.51 (1H, H$_6$ *exo*), 1.49 (1H, P2CH_2), 1.43 (1H, Cy−H$_1^{\alpha}$), 1.36 (1H, H$_{14}$), 1.27 (1H, H$_{16}$), 1.06 (1H, H$_8$), 0.86 (1H, P2CH_2), 0.83 (1H, P1CH_2). ^{13}C NMR (C$_6$D$_6$, 150.9 MHz, 303 K): δ 83.1 (s, $^1J_{\mathrm{C-H}} = 155 \pm 1$ Hz, C$_2$), 75.9 (d, $^3J_{\mathrm{P1-C}} = 1.4$ Hz, $^1J_{\mathrm{C-H}} = 164 \pm 1$ Hz, C$_{12}$), 63.3 (d, $^2J_{\mathrm{P1-C}} = 31.1$ Hz, $^1J_{\mathrm{C-H}} = 150 \pm 2$ Hz, C$_{11}$, *cis,trans* to P), 50.1 (d, $^2J_{\mathrm{P-C}} = 3.5$ Hz, $^1J_{\mathrm{C-H}} = 154 \pm 1$ Hz, C$_{13}$, *cis,cis* to P), 48.4 (m, $^1J_{\mathrm{C-H}} = 142 \pm 2$ Hz, C$_3$, *cis,cis* to P), 47.8 (m, $|^2J_{\mathrm{P1-C}} + {}^2J_{\mathrm{P2-C}}| \approx 28$ Hz, $^1J_{\mathrm{C-H}} = 142 \pm 2$ Hz, C$_1$, *cis,trans* to P), 45.0 (dd, $^1J_{\mathrm{P-C}}/^3J_{\mathrm{P-C}} = 14.1/2.4$ Hz, $^1J_{\mathrm{C-H}} = 122 \pm 1$ Hz, Cy−C$_1^{\alpha}$), 40.5 (d, $^1J_{\mathrm{P-C}} = 19.9$ Hz, $^1J_{\mathrm{C-H}} = 124 \pm 2$ Hz, Cy−C$_1^{\beta}$), 39.6 (dd, $^1J_{\mathrm{P1-C}}/^3J_{\mathrm{P2-C}} = 23.7/1.9$ Hz, $^1J_{\mathrm{C-H}} = 132 \pm 2$ Hz, C$_{15}$), 39.2 (d, $^1J_{\mathrm{P-C}} = 6.2$ Hz, $^1J_{\mathrm{C-H}} = 122 \pm 1$ Hz, Cy−C$_1^{\gamma}$), 36.1 (s, $^1J_{\mathrm{C-H}}$

$= 125 \pm 1$ Hz, C_4), 31.4 (d, C_5), 31.0 (d, $^2J_{P-C} = 2.1$ Hz, Cy−C_2^{α}), 30.8 (d, $^4J_{P-C} = 5.8$ Hz, C_7), 30.6 (d, $^2J_{P-C} = 4.3$ Hz, Cy−C_2^{β}), 29.4 (d, $^2J_{P1-C} = 14.6$ Hz, C_{14}), 29.3 (d, $^2J_{P1-C} = 2.7$ Hz, Cy−C_2 adjacent to cyclohexenylic moiety), 28.9 (d, Cy−C_2^{γ}), 28.6 (d, $^2J_{P-C} = 5.3$ Hz, Cy−C_2^{δ}), 28.5 (d, $^2J_{P-C} = 2.3$ Hz, Cy−C_2^{ϵ}), 28.4 (d, $^2J_{P-C} = 11.4$ Hz, Cy−C_3^{α}), 28.2 (d, $^3J_{P-C} = 10.5$ Hz, Cy−C_3^{β}), 28.2 (d, $^3J_{P-C} = 10.2$ Hz, Cy−C_3^{γ}), 28.1 (d, $^3J_{P-C} = 2.5$ Hz, C_8), 28.0 (d, $^3J_{P-C} = 6.5$ Hz, Cy−C_3^{δ}), 27.7 (d, $^3J_{P-C} = 7.2$ Hz, Cy−C_3^{ϵ}), 27.5 (d, $^3J_{P-C} = 6.4$ Hz, Cy−C_3^{δ}), 27.2 (dd, $^2J_{P1-C}/^4J_{P2-C} =$11.8/3.1 Hz, C_{16}), 27.1 (s, Cy−C_4^{α}), 27.0 (s, Cy−C_4^{β}), 26.9 (s, Cy−C_4^{γ}), 26.2 (dd, $^1J_{P2-C}/^3J_{P1-C} = 21.8/8.9$ Hz, P2CH$_2$), 25.9 (m, C_6), 23.1 (dd, $^2J_{P2-C}/^2J_{P1-C} = 5.7/2.9$ Hz, $^1J_{C-H} = 128 \pm 1$ Hz, PCH$_2$$CH_2$), 18.1 (d, $^1J_{P1-C} = 12.1$ Hz, $^1J_{C-H} = 125 \pm 1$ Hz, P1CH$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 243.0 MHz, 303 K): δ 72.9 (d, $^2J_{P1-P2} = 34.3$ Hz, P1), 27.7 (d, $^2J_{P1-P2} = 34.3$ Hz, P2).

[κ^2P,P′-{(η^3-C_6H_8)CyP(CH_2)$_4$PCy$_2$}Ru(η^3-C_8H_{13})] (8d). **4** (208 mg, 0.651 mmol) and **1d** (295 mg, 1 equiv) were dissolved in hexane (30 mL) and heated to 50 °C (bath temperature). The almost colorless solution turned yellow after 10 min and darkened quickly to brown. After 6 h, the $^{31}P\{^1H\}$ NMR of a sample taken from the homogeneous solution still showed the presence of large amounts of free phosphine. After a total reaction time of 18 h, $^{31}P\{^1H\}$ NMR indicated almost quantitative conversion. The reaction mixture was cooled to room temperature and concentrated in vacuo to 5 mL. The solution was stored at 4 °C for 10 days, affording a bright orange solid, which was filtered, washed with hexane (2 × 1 mL), and dried in vacuo. The filtrate was evaporated to dryness to give a brown residue from which additional crops of **8d** could be isolated by dissolving it in 2 mL of pentane and storing the solution at 4 °C for 4 weeks. Yield: 135 mg (0.205 mmol, 32%). Mp: 150 °C (dec 160 °C). Anal. Found: C, 65.94; H, 9.63; P, 9.49. Calcd for $C_{36}H_{62}P_2Ru$: C, 65.72; H, 9.50; P, 9.42.

EI-MS (temperature of vaporization: 160 °C): $m/e = 658$ ($M^{\bullet+}$, 16), 548 ($[Ru_1]^+$, 29), 460 ($[Ru_1]^+$, 26), 350 ($[Ru_1]^+$, 22), 198 ($(C_6H_{11})_2PH^+$, 13), 78 ($C_6H_6^+$, 100), 55 ($C_4H_7^+$, 76). IR (KBr disk): 3009 w; 2966 s; 2927 s; 2847 s; 2815 s; 1448 s; 1409 s; 1347 s; 1313 s; 1296 m; 1262 m; 1236 m; 1216 m; 1174 m; 1149 m; 1123 w; 1069 w; 1029 w; 1001 m; 991 w; 888 m; 847 m; 823 m; 807 w; 758 w; 727 w; 667 w; 527 w; 489 m; 466 m cm^{-1}. ^1H NMR (C_6D_6, 400.1 MHz, 300 K): δ 5.56 (m, 1H, H_{12}), 4.09 (m, $J \approx 6.9$ Hz, 2H), 3.90 (m, $J = 9.8/7.3/2.0$ Hz, 2H), 3.27 (m, $J \approx 12.9/2.5$ Hz, $|J| = 5.8$ Hz, 2H), 2.75−0.92 (51H), 0.86 (m, $|J| \approx 11.1$, 4H). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz, 300 K): δ 77.6 (vt, $|^3J_{P1-C} + {}^3J_{P2-C}| = 10.7$ Hz, 1C), 66.7 (d, $^2J_{P1-C} = 7.2$ Hz, 1C), 61.2 (dd, $^1J_{P2-C}/^3J_{P1-C} = 11.1/4.7$ Hz, 1C), 59.4 (dd, $J_{P-C} = 20.4/5.3$ Hz, 1C), 56.5 (partly obscured dd, $J_{P-C} = 6.2$ Hz, 1C), 44.2 (dd, $J_{P-C} = 19.5/1.5$ Hz, 1C), 41.7 (dd, $J_{P-C} = 7.9/3.5$ Hz, 1C), 41.5 (dd, $J_{P-C} = 8.5/2.7$ Hz, 1C), 41.3 (dd, $J_{P-C} = 13.7/5.5$ Hz, 1C), 37.5 (d, $J_{P-C} = 18.6$ Hz, 1C), 37.0 (d, 1C), 36.0 (dd, $J_{P-C} \approx 23.7/3.5$, 1C), 35.9 (d, $J_{P-C} \approx 2.5$ Hz, 1C), 35.2 (d, $J_{P-C} = 7.4$ Hz, 1C), 33.8 (dd, $J_{P-C} \approx 6.8/2.2$ Hz, 1C and partly obscured d, 1C), 31.6 (s, 1C), 31.4 (2 d, $J_{P-C} = 3.5$ Hz and $J_{P-C} = 3.8$ Hz, 2C), 31.2 (d, $J_{P-C} = 1.8$ Hz, 1C), 31.1 (d, $J_{P-C} = 1.3$ Hz, 1C), 30.7 (d, $J_{P-C} = 4.0$ Hz, 1C), 30.5 (partly obscured dd, $J_{P-C} = 3.3$ Hz, 1C), 30.2 (d, $J_{P-C} = 5.1$ Hz, 1C), 29.8 (d, $J_{P-C} = 2.8$ Hz, 1C), 29.6 (d, $J_{P-C} = 2.6$ Hz, 1C), 29.2−27.7 (m, 6C), 27.2 (s, 1C), 27.1 (s, 1C), 27.0 (s, 1C), 26.6 (s, 1C). $^{31}P\{^1H\}$ NMR (C_6D_6, 162.0 MHz, 300 K): δ 73.0 (d, $J_{P1-P2} = 29.6$ Hz, P1), 9.2 (d, $J_{P1-P2} = 29.6$ Hz, P2).

Catalytic Reactions. Thermal dehydrogenation or transfer−dehydrogenation was performed with different reaction systems. Type I (standard dehydrogenation): 0.015−0.040 mmol of catalyst precursor was weighed into a Schlenk tube (50 mL) and dissolved in 5−15 mL of coa. The tube was equipped with a reflux condenser and connected to a gas bubbler. An inert atmosphere was ensured throughout the experiment by passing a gentle stream of argon over the reaction mixture on top of the condenser. In a typical experiment, the solution was heated to reflux temperature of coa (151 °C) with the oil bath set at 170 °C for 48 h. After cooling, metal-containing species were removed by passing the solution through a short pad of silica or by Kugelrohr distillation.[26] The clear colorless liquid was quantitatively analyzed by gas chromatography using cyclohexane as an internal standard.

Type II (time-dependence monitoring) was carried out as for type I, except that the catalyst solution was prepared in a 50 mL three-necked round-bottomed flask equipped with an argon inlet, a reflux condenser, and a rubber septum seal. Small samples (0.5 mL) of the reaction mixture were withdrawn periodically through the septum using a 1 mL gastight Hamilton syringe and immediately frozen at −78 °C. Workup and analysis were performed as for type I.

Type III (gas-phase investigations) was carried out as for type I, except that the Schlenk tube was connected to a gas sampling tube which was especially designed to fit a modified Varian MAT CH7 for quantitative GC/MS analyses. The reaction mixture was frozen at −78 °C and the whole apparatus evacuated before starting the reaction.

Type IV (standard transfer−dehydrogenation) was carried out as for type I, but the hydrogen acceptor tbe was added in a molar ratio of 1:5 relative to coa. The resulting mixture was heated to 120 °C (bath temperature) for 48 h.

Attempted C−H Activation in the Presence of Supercritical CO_2. The catalyst precursor **5** was dissolved in coa, and the resulting homogeneous solution was transferred into a stainless steel autoclave ($V = 225$ mL). The autoclave was pressurized with CO_2 and then heated to 100 °C, resulting in a total pressure of approximately 200 bar. After cooling to room temperature, the reactor was carefully vented, whereby the volatiles were passed through a cold trap held at −50 °C. The collected liquid was quantitatively analyzed by gas chromatography using cyclohexane as an internal standard. In one experiment using **5c** as the precursor, small amounts (<10 mg) of a solid were carefully recovered from the autoclave in a glovebox and submitted to FT-IR analysis.

X-ray Crystal Structure Analysis. The crystals were mounted in a cold nitrogen stream at −90 °C. For the data collection a Nonius CAD4 diffractometer (compound **5b**) and a Nonius KappaCCD (compound **8c**) using graphite-monochromated Mo Kα radiation was used. Data were corrected for Lorentz and polarization effects.[35] No absorption correction was made. The structures were solved by direct methods (SHELXS[36]) and refined by full-matrix least-squares techniques against F^2 (SHELXL-93[37]). For **8c** all hydrogen atoms were located by difference Fourier synthesis and refined isotropically. The hydrogen atoms for **5b** were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for 5b:[38] $C_{34}H_{62}P_2Ru$, $M_r = 633.85$ g mol^{-1}, colorless prism, size 0.32 × 0.32 × 0.20 mm^3, monoclinic, space group $C2/c$, $a = 29.992(4)$ Å, $b = 12.436(3)$ Å, $c = 18.197(3)$ Å, $\beta = 108.65(1)°$, $V = 6430(2)$ Å^3, $T = -90$ °C, $Z = 8$, $\rho_{calcd} = 1.309$ g cm^{-3}, μ (Mo Kα) = 6.08 cm^{-1}, $F(000) = 2720$, 7453 reflections in $h(-38/0)$, $k(-16/0)$, $l(-22/23)$, measured in the range $2.27° \le \theta \le 27.41°$, 7316 independent reflections, $R_{int} =$

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(37) Sheldrick, G. M. University of Göttingen, Germany, 1993.

(38) Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-410550 (**5b**) and CSD-410551 (**8c**), the names of the authors, and the journal citation.

0.031, 4574 reflections with $F_o > 4\sigma(F_o)$, 334 parameters, $R_{obs} = 0.049$, $wR^2_{obs} = 0.104$, GOOF = 1.129, largest difference peak and hole 0.336/−0.599 e Å^{-3}.

Crystal Data for 8c:[38] $C_{35}H_{60}P_2Ru$, $M_r = 643.84$ g mol^{-1}, colorless prism, size 0.20 × 0.20 × 0.20 mm^3, monoclinic, space group $P2_1/c$, $a = 15.9384(5)$ Å, $b = 11.2544(5)$ Å, $c = 18.8428(8)$ Å, $\beta = 107.963(2)°$, $V = 3215.2(2)$ Å^3, $T = -90$ °C, $Z = 4$, $\rho_{calcd} = 1.330$ g cm^{-3}, μ (Mo Kα) = 6.1 cm^{-1}, $F(000) = 1376$, 8490 reflections in $h(-17/17)$, $k(0/12)$, $l(-20/20)$, measured in the range 3.15° ≤ θ ≤ 23.25°, 4440 independent reflections, $R_{int} = 0.0382$, 3388 reflections with $F_o > 4\sigma(F_o)$, 583 parameters, $R_{obs} = 0.032$, $wR^2_{obs} = 0.071$, GOOF = 0.988, largest difference peak and hole 0.336/−0.476 e Å^{-3}.

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Supporting Information Available: A listing of crystal data and positional parameters for complexes **5a** and **8c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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