Decarbonylation of Aryl Ketones Mediated by Bulky Cyclopentadienylrhodium Bis(ethylene) Complexes

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The cleavage of C−C bonds of diaryl ketones and aryl alkyl ketones mediated by bulky (1,2,4-triisopropyl-3,5-dimethylcyclopentadienyl)rhodium bis(ethylene) (**1**) and (1,2,4-tri-*tert*-butylcyclopentadienyl)rhodium bis(ethylene) (**2**) is reported. The reactions using **2** proceed at 120−150 °C, and the products of the decarbonylation are the (tri-*tert*-butylcyclopentadienyl)rhodium carbonyl dimer **4**, the carbonyl ethylene complex **7**, biphenyls (from benzophenones), and toluenes (from acetophenones). Use of β-phenylpropiophenone as substrate results initially in dehydrogenation to form the η^4-enone complex **13**, followed by decarbonylation at higher temperatures to yield stilbene.

Introduction

Transition-metal-mediated cleavage of C−C bonds is substantially more difficult than C−H bond cleavage for both kinetic and thermodynamic reasons and represents a significant challenge.[1] Success in activating C−C bonds has often relied on use of special substrates. There are numerous reports of metal-mediated cleavage of C−C bonds of molecules possessing significant ring strain, particularly cyclopropane derivatives.[1e,2,3] Use of directing groups to facilitate access of the metal center to the C−C bond has been a successful strategy. Prominent examples include catalytic C−C bond cleavage in 2-amino-3-picolylimines[1d,f,4] and stoichiometric and catalytic C−C bond cleavage in phosphine-based pincer complexes.[1a,g,5] Aromatization and cooperative effects in metal clusters have also been used to facilitate C−C bond cleavage.[6] Several reports describing the C−C bond cleavage in nitriles have appeared recently.[7]

The cleavage of C(O)−C_α bonds of ketones by transition metals[8] has generally been confined to activated systems such as strained cyclic ketones,[8a−f] diketones,[8g−i] alkynyl ketones,[8j] and functionalized ketones or their derivatives possessing a chelating group that directs the bond activation step.[8k,l] Relatively few examples of C−C bond cleavage of nonactivated ketones have been reported. Ito, Murakami, et al. have demonstrated that cyclopentanones and cyclododecanone upon thermolysis (110−150 °C, days) in the presence of stoichiometric $(PPh_3)_3RhCl$ yield cyclobutanes and cycloundecane.[8a,b] Decarbonylation of cyclohexanone[8m] and cleavage of acetone to produce methane have also been reported.[8n] The protocol developed by Jun[1d,f,4] results in the cleavage of C−C bonds in nonactivated ketones; however, the actual cleavage step occurs in a chelate-activated picolylketimine.

Much of our recent work on C−H bond activation and incorporation of C−H activation processes into catalytic cycles has involved the use of Cp*Rh(I) and Cp*Co(I) moieties.[9] Jones has shown that $Cp^*Rh(C_2H_4)_2$ and $Cp^*Co(C_2H_4)_2$ can be used to cleave C_{sp^2}−C_{sp^2} bonds in

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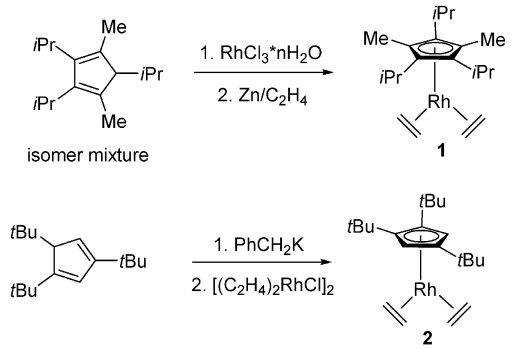
Scheme 1



strained hydrocarbons.[10] Spurred by the results of these studies, we have investigated the possibility of using bulky cyclopentadienylrhodium(I) fragments generated from thermolysis of bis(ethylene) complexes for cleavage of C−C bonds of aryl ketones. We report here the studies of these cleavage reactions employing (1,2,4-triisopropyl-3,5-dimethylcyclopentadienyl)rhodium bis(ethylene) (**1**) and (1,2,4-tri-*tert*-butylcyclopentadienyl)rhodium bis(ethylene) (**2**).

Results and Discussion

Synthesis of the Rhodium Complexes. Two methods summarized in Scheme 1 were used to synthesize the bulky cyclopentadienylrhodium ethylene complexes. (1,2,4-Triisopropyl-3,5-dimethylcyclopentadienyl)rhodium bis(ethylene) (**1**) was prepared in a two-step synthesis starting from $RhCl_3 \cdot nH_2O$ in 63% yield. (1,2,4-Tri-*tert*-butylcyclopentadienyl)rhodium bis(ethylene) (**2**) was prepared in good yield (76%) from chlorobis(ethylene)rhodium dimer and (1,2,4-tri-*tert*-butylcyclopentadienyl)potassium. Both substances are yellow solids and stable under inert atmosphere at room temperature.

Crystals of **1** suitable for an X-ray structure determination were grown from acetone solution at −30 °C. The ORTEP diagram of **1** is shown in Figure 1. The C═C bond lengths of complexed ethylene in **1** are 1.387(6) and 1.376(4) Å, in the same range as for other cyclopentadienylrhodium ethylene complexes (typically 1.36−1.43 Å)[11] but elongated compared to free ethylene (1.339 Å).[12] The Rh−ethylene (Rh−C1 and Rh−C2) distances of ca. 2.1 Å are close to values reported in the literature.[11] The rhodium center is partially shielded by the isopropyl groups that are situated perpendicular to the cyclopentadiene ring.

Several rhodium-containing intermediates and products of the decarbonylation reactions (see below) were prepared independently and characterized (Scheme 2).

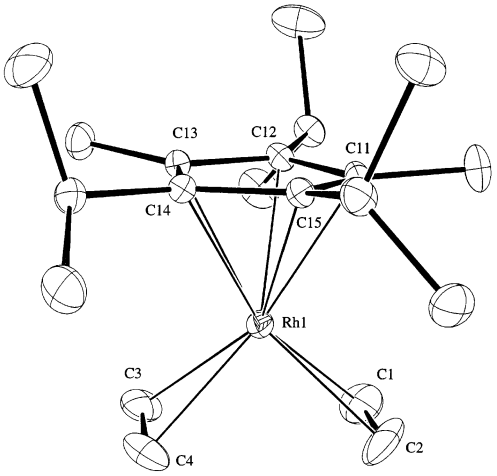


Figure 1. ORTEP view of **1**. Selected interatomic distances (Å): Rh(1)−C(1) = 2.101(3), Rh(1)−C(2) = 2.118(3), Rh(1)−C(3) = 2.1271(24), Rh(1)−C(4) = 2.1314(25), C(1)−C(2) = 1.387(6), C(3)−C(4) = 1.376(4).

The reaction of ethylene complexes **1** and **2** with *tert*-butyl vinyl ether at 120 °C in hexanes or without solvent affords the carbonyl dimers **3** and **4** as intensely blue-violet crystalline materials. Isobutylene and methane were observed in the crude reaction mixtures by NMR spectroscopy. In the case of the reaction of **2**, the main byproduct in the crude reaction mixture was identified as the dicarbonyl complex **5**, independently synthesized from chlorodicarbonylrhodium dimer and (1,2,4-tri-*tert*-butylcyclopentadienyl)potassium. Like $Cp^*Rh(CO)_2$ (**6**),[13] **5** slowly loses CO under vacuum, forming **4**. The reaction of **2** with CO at 70 °C yields the carbonyl ethylene complex **7**. At 80 °C, the substitution is nonselective and substantial amounts of **5** are formed. Complex **7** is unstable at room temperature in solution and slowly loses ethylene, forming the highly colored carbonyl dimer **4**.

Decarbonylation of Ketones Mediated by 1 and 2. The thermolysis of $Cp^*Rh(C_2H_4)_2$ (**8**)[14] and $Cp^*Rh(C_2H_3TMS)_2$ (**9**)[9a] with 3-(trifluoromethyl)acetophenone in C_6D_{12} at 120 °C produced complicated mixtures containing multiple Cp* signals, and mostly ketone ortho-alkylation products were observed. Thermolysis of $Cp^*Rh(C_2H_4)_2$ with 4,4′-dimethylbenzophenone also yielded ortho-alkylation products in a mixture with 4,4′-dimethylbiphenyl. Multiple Cp* signals were observed in the reaction mixture by ^1H NMR spectroscopy. On the other hand, the corresponding reactions using the more hindered derivative **1** afforded dimer **3** and decarbonylation products, biphenyls or toluenes. Since the NMR spectra of these reaction mixtures were complicated in the alkyl region (multiple Me and *i*-Pr signals), the tri-*tert*-butyl-substituted complex **2** was synthesized and tested in the decarbonylation reactions. Qualitative comparison of the rate of decarbonylation (3.4 equiv of 3-methylbenzophenone, 0.1 M Rh complex in C_6D_{12}, 120 °C) showed that both Rh complexes decarbonylate this substrate at about equal rates (10−15% conversion to the carbonyl dimers **3** and **4** in 1 h). As a consequence,

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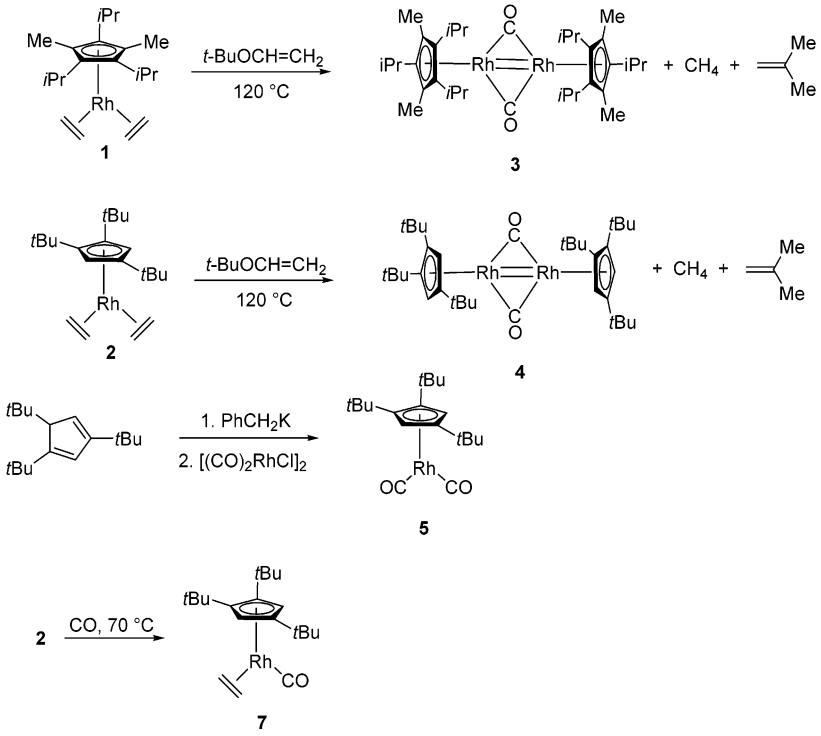
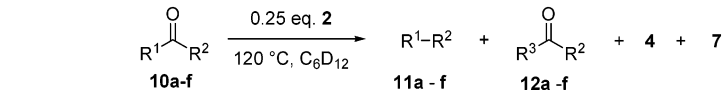
Scheme 2



Scheme 3



10a, **11a** $R^1 = R^2 = (3,5)\text{-}(CF_3)_2C_6H_3$
10b, **11b** $R^1 = R^2 = 3\text{-}CF_3C_6H_4$
10c, **11c** $R^1 = R^2 = C_6H_5$
10d, **11d** $R^1 = R^2 = 4\text{-}CH_3C_6H_4$
10e, **11e** $R^1 = 4\text{-}CF_3C_6H_4$, $R^2 = CH_3$
10f, **11f** $R^1 = C_6H_5$, $R^2 = CH_3$

12b $R^3 = 2\text{-Et-}5\text{-}CF_3C_6H_3$
12c $R^3 = 2\text{-Et}C_6H_4$
12d $R^3 = 2\text{-Et-}4\text{-Me}C_6H_3$
12e $R^3 = 2\text{-Et-}4\text{-}CF_3C_6H_3$ and $2,6\text{-}Et_2\text{-}4\text{-}CF_3C_6H_2$
12f $R^3 = 2\text{-Et}C_6H_4$

further experiments were carried out using **2** which gave substantially simplified NMR spectra.

Several benzophenones and acetophenones were decarbonylated using complex **2** in cyclohexane-d_{12}. Reactions were monitored by ^{1}H NMR spectroscopy, and conversions were determined by reference to a capillary insert containing a mixture of $C_2H_2Cl_4$ and $C_2D_2Cl_4$. In addition, two preparative thermolyses were carried out, from which decarbonylation products were isolated. Scheme 3 illustrates the general reactions observed. Table 1 summarizes the in situ experiments. Reactions were carried out at 120 °C with 0.05 mmol of **2** and 0.2 mmol of ketone **10**. The extent of decarbonylation is best quantitatively monitored by watching the formation of rhodium carbonyl complexes **4** and **7**, although the biaryls or methyl arenes **11** can also be detected. In the early stages of reaction, the ethylene carbonyl complex **7** is the major product, but at 120 °C this complex converts to the carbonyl dimer **4**. Except in the case of **10a**, in addition to the decarbonylated organic products, ortho ethylation of the aryl ring occurs via insertion of ethylene into the ortho C−H bond. We have reported similar ortho-alkylation reactions using Cp*Rh(C_2H_3-Si(CH_3)$_3$) as a catalyst.[9b]

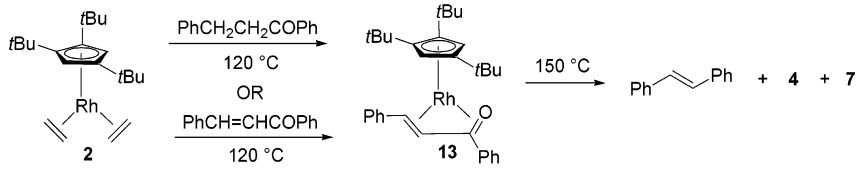
Entries 1−3 summarize the results for 3,5,3′,5′-tetrakis(trifluoromethyl)benzophenone (**10a**). As noted above, no ortho-ethylation product **12** is observed, no doubt due to the presence of CF_3 groups adjacent to each ortho C−H bond. At 7 h complexes **4** and **7** are present at approximately equal concentrations, but at 26 h

Table 1. Decarbonylation of Ketones Mediated by 2[a]

			conversn (%)[b] to			
entry	ketone	time, h	**12**	**4**	**7**	**4** + **7**
1	**10a**	7	0	28	22	50
2	**10a**	13	0	53	21	74
3	**10a**	26	0	68	<5	73
4	**10b**	1	25	14	31	45
5	**10b**	3	35	48	25	73
6	**10b**	10.5	35	74	11	85
7	**10c**	1	30	15	23	38
8	**10c**	3	42	42	15	57
9	**10c**	10.5	42	61	<5	66
10	**10d**	1	28	16	20	36
11	**10d**	3	37	33	11	44
12	**10d**	10.5	37	50	5	55
13	**10e**	1	6	<2	<2	ND
14	**10e**	7	20	11	11	22
15	**10e**	36	27	34	<2	36
16	**10f**	1	<2	<2	<2	ND
17	**10f**	7	ca. 10	<2	<2	ND
18	**10f**	36	18	24	<2	ca. 26

[a] Conditions: 0.5 mL of C_6D_{12}, 0.05 mmol of **2**, 0.2 mmol of **10**, 120 °C. [b] Conversion to **12** with respect to the initial amount of **10** and to **4** and **7** with respect to the initial amount of **2**.

Scheme 4



virtually all of **7** has been converted to **4**. Decarbonylation is essentially complete after 13 h.

Entries 4−6 summarize results for 3,3′-bis(trifluoromethyl)benzophenone (**10b**). In this case a significant amount of ortho-ethylation product **12b** is observed. After 1 h, ca. 45% decarbonylation has occurred, with the major Rh product being the mononuclear complex **7**. Decarbonylation proceeds to ca. 85% in 10.5 h, with dimer **4** now being the major Rh carbonyl species. A preparative-scale reaction was carried out in toluene (135 °C, 23 h), and the biaryl **11b** was isolated in ca. 82% yield.

Entries 7−9 and 10−12 summarize results for benzophenone (**10c**) and 4,4′-dimethylbenzophenone (**10d**), respectively. The behavior of these ketones is similar to that of **10a**. For example, after 3 h ca. 50% decarbonylation has occurred and ca. 40% ortho-ethylated product is observed. In a preparative-scale reaction employing **10d** in cyclohexane-d_{12} (120 °C, 17 h), 4,4′-dimethylbiphenyl (**11d**) was isolated in 62% yield along with the ortho-ethylated product **12d** in 66% yield. Only a trace (<2%) of an impurity tentatively assigned as 2-ethyl-4,4′-dimethylbiphenyl (arising from the decarbonylation of **12d**) was observed.

Entries 13−15 and 16−18 summarize results for 4-(trifluoromethyl)acetophenone (**10e**) and acetophenone (**10f**). The decarbonylations are substantially slower than in the case of benzophenones, and the conversions attained are lower. For example, 7 h is necessary to obtain 22% conversion in the case of **10e**, and in the case of **10f** after 36 h ca. 26% conversion was observed. The thermolysis of acetophenones **10e** and **10f** was studied also at 150 °C. After 4 h (0.05 mmol of **2**, 0.2 mmol of ketone, 0.5 mL of C_6D_{12}) 47% and 38% conversion to **4** was observed, respectively. Only trace amounts of **7** were observed.

For benzophenones, the reaction rate is not strongly dependent on the electronic properties of the aryl group. However, in the case of acetophenones, the decarbonylation is substantially faster for the electron-withdrawing trifluoromethyl-substituted substrate **10e**. The thermolysis of **2** and benzophenone (**10c**) was carried out at 120 °C using two different ketone concentrations. As expected, the reaction is faster if a higher concentration of benzophenone is used (ethylene dissociation is reversible;[9] see Scheme 5). Using 3.5 equiv of ketone (0.05 mmol of **2**, 0.5 mL of C_6D_{12}), 10% conversion to **4** and 23% conversion to **7** was observed in 1 h. If 10 equiv of ketone was used, 27% conversion to **4** and 23% conversion to **7** was observed in 1 h.

While decarbonylations of acetophenones and benzophenones occur at 120 °C, we were surprised to find that thermolysis of **2** and β-phenylpropiophenone at 120 °C did not yield any carbonyl dimer **4**. Instead, slow formation (50% conversion, 35 h) of the enone (chalcone) complex **13** is observed (Scheme 4). Complex **13** exhibits three inequivalent *tert*-butyl resonances at δ 0.69, 1.17, and 1.41 and characteristic signals for the vinyl hydrogens of the bound enone at δ 3.4 (d, $J_{H-H} = 8.3$ Hz) and 5.95 (dd, $J_{H-H} = 8.3$ Hz, $J_{H-Rh} = 0.8$ Hz). While Cp*Rh-($C_2H_3SiMe_3$)$_2$ is known to catalyze intramolecular hydrogen transfer,[9c] formation of **13** is the first observation of intermolecular hydrogen transfer mediated by these systems. Further heating of the reaction mixture at 150 °C results in C−C activation and formation of stilbene along with complexes **4** and **7**. Thermolysis of **2** with chalcone at 120 °C results in clean formation of **13** and serves to confirm its structural assignment. Furthermore, suitable crystals for an X-ray structure determination were grown from acetone solution of **13** at −30 °C. The ORTEP diagram of **13** is shown in Figure 2. The enone binds to the rhodium fragment in an η^4 fashion through the O(1)−C(2)−C(3)−C(4) atoms. In comparison to free chalcone,[15] the C(2)−O(1) bond is elongated from 1.204(6) to 1.304(4) Å and C(3)−C(4) from 1.319(6) to 1.429(5) Å. The length of the C(2)−C(3) bond is somewhat shortened from 1.478(6) to 1.437(5) Å. The enone moiety is almost planar (O(1)−C(2)−C(3)−C(4) = −2.7°). Iron and ruthenium enone complexes are common and have been crystallographically characterized;[16] however, no rhodium(I) η^4-enone complexes appear to have been crystallographically characterized. An η^4-acrolein−rhodium complex has been spectroscopically characterized.[17]

Mechanistic Considerations. At this stage only a somewhat speculative discussion of the reaction mechanism is possible (Scheme 5). Complexation of the ketone to the rhodium fragment must precede the C−C activation step. The isolation of intermediate **13** prior to decarbonylation and formation of stilbene suggests that in the case of benzophenone or acetophenone the complex formed prior to C−C bond cleavage is the enone-type complex **14**, involving η^2 coordination of the arene. In fact, the Cp*Rh complex **18**, exhibiting this mode of coordination, has been isolated and characterized.[9b] From **14** oxidative addition would yield **15**, which upon deinsertion would produce **16**.[18] Reductive elimination from **16** (possibly preceded by CO loss)[19] leads to hydrocarbon product and the rhodium species **17**, which can form **4** and **7**. Complex **7** is relatively unstable and upon prolonged heating loses ethylene and

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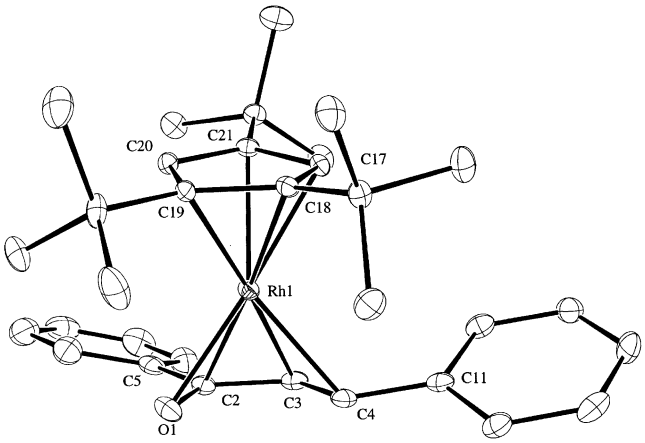
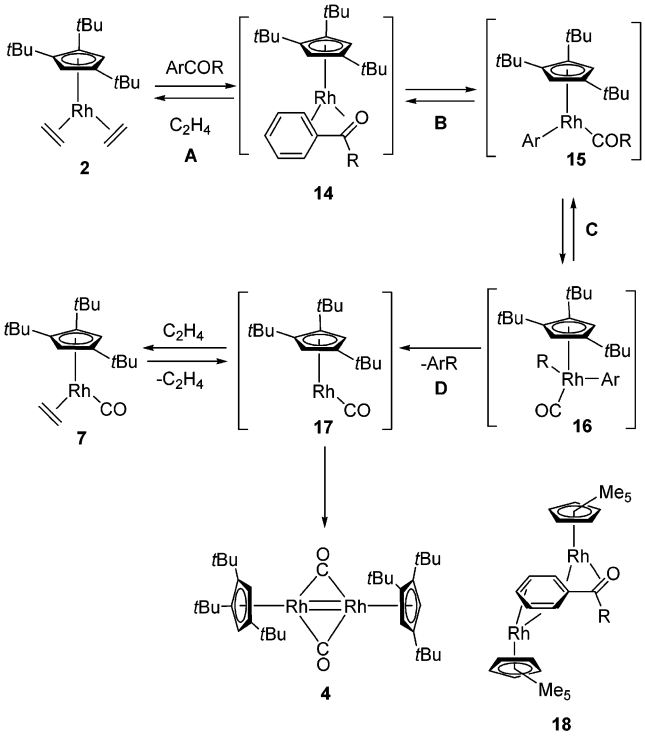


Figure 2. ORTEP view of **13**. Selected interatomic distances (Å) and angles (deg): C(2)−O(1) = 1.304(4), C(3)−C(4) = 1.429(5), Rh(1)−O(1) = 2.1663(23), Rh(1)−C(2) = 2.137(3), Rh(1)−C(3) = 2.137(4), Rh(1)−C(4) = 2.174(3), C(2)−C(3) = 1.437(5); O(1)−C(2)−C(3)−C(4) = −2.7.

Scheme 5



forms **4**. Species of the type **16** have been shown to be resting states in catalytic hydroacylation reactions of olefins by aryl aldehydes, which suggests the reversibility of steps **B** and **C**.[20] In the hydroacylation reactions, catalyst deactivation occurs by formation of $[Cp^*RhCO]_2$, which is also consistent with Scheme 5.

Summary

The cleavage of C−C bonds in diaryl and aryl alkyl ketones mediated by bulky cyclopentadienylrhodium ethylene complexes **1** and **2** has been investigated. The reactions proceed at 120−150 °C, and the initial product of the decarbonylation is the carbonyl ethylene complex **7**, which is converted to the cyclopentadienylrhodium carbonyl dimer **4.** The organic products of the reaction are biphenyls (from benzophenones) or toluenes (from acetophenones). If ketones possessing β-hydrogens are used as substrates, dehydrogenation to unsaturated ketones precedes the C−C activation. The rhodium η^4-enone complex **13** has been isolated and crystallographically characterized. Future investigations will involve attempts to develop catalytic reactions and in-depth studies of the reaction mechanism.

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Experimental Section

General Considerations. All the operations related to catalysts were carried out under an argon atmosphere using standard Schlenk techniques. The ^{1}H and ^{13}C spectra were recorded using Bruker 300, 400, or 500 MHz spectrometers and are referenced against residual solvent peaks (^{1}H, ^{13}C). Flash chromatography was performed using 60 Å silica gel (SAI). Elemental analyses were performed by Atlantic Microlab Inc. of Norcross, GA. Yields in the preparative decarbonylation reactions (leading to **4**, **7**, **11**, and **12**) were calculated with respect to **2**.

Materials. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through alumina columns under an argon or nitrogen atmosphere. NMR solvents were vacuum-transferred from P_2O_5 and degassed by repeated freeze−pump−thaw cycles. The following starting materials were made using literature procedures: 1,2,4-triisopropyl-3,5-dimethylcyclopentadiene,[21] 1,2,4-tri-*tert*-butylcyclopentadiene,[22] benzylpotassium,[23] and chlorobis(ethylene)rhodium dimer.[24]

1,2,4-*i*Pr$_3$-3,5-Me$_2$CpRh(C$_2$H$_4$)$_2$ (1). To a solution of $RhCl_3 \cdot nH_2O$ (0.66 g, 2.31 mmol, Next Chimica) in methanol (30 mL) was added 1,2,4-triisopropyl-3,5-dimethylcyclopentadiene (1.20 g, 5.45 mmol). The mixture was refluxed for 66 h. Methanol was evaporated, and the residue was suspended in toluene and evaporated (2 × 30 mL). After that, the residue was suspended in hexanes and filtered. After drying, a reddish yellow solid (0.90 g) was obtained. This material (mostly (1,2,4-triisopropyl-3,5-dimethylcyclopentadienyl)rhodium dichloride dimer) was used further without additional purification. The material obtained as above (1.23 g) was mixed with Zn powder (2.50 g, 38.2 mmol, Aldrich) and THF (20 mL). Ethylene was slowly purged through the magnetically stirred mixture for 15 h. The color changed from reddish to blue to violet. The solvent was evaporated, the residue was extracted with pentane (2 × 10 mL), and the extracts were filtered through a pad of alumina (3 × 2.2 cm) in pentane. The solution was evaporated and the residue crystallized from acetone at −78 °C. Two crops of the product were collected: (1) 0.57 g of dark yellow crystals; (2) 0.19 g of dark yellow crystals. Total yield: 0.76 g (63.4% from rhodium trichloride). ^{1}H NMR (C_6D_6): δ 2.67 (septet, 2H; J = 7.2 Hz); 2.48 (septet, 1H; J = 7.2 Hz); 2.31−2.14 (m, 4H; complexed ethylene); 1.51 (s, 6H); 1.48−1.35 (m, 4H; complexed ethylene); 1.32 (d, 6H; J = 7.2 Hz); 1.25 (d, 6H; J = 7.2 Hz); 1.20 (d, 6H; J = 7.2 Hz). ^{13}C{^{1}H} NMR (C_6D_6) δ 110.3 (d, J_{Rh-C} = 4.9 Hz); 109.6 (d, J_{Rh-C} = 4.4 Hz); 94.3 (d, J_{Rh-C} = 4.3 Hz); 43.1 (d, J_{Rh-C} = 13.6 Hz); 26.5; 26.1; 24.5; 24.2; 24.1; 10.6. Anal. Calcd for $C_{20}H_{35}Rh$: C, 63.48; H, 9.32. Found: C, 63.54; H, 9.55. The structure was verified by X-ray crystallography.

1,2,4-*t*Bu$_3$CpRh(C$_2$H$_4$)$_2$ (2). To a solution of 1,2,4-tri-*tert*-butylcyclopentadiene (0.933 g, 4.0 mmol) in THF (10 mL) was added a solution of benzylpotassium (0.535 g, 4.1 mmol) in

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THF (10 mL) at 0 °C. Benzylpotassium has an intense red color, and the exact stoichiometry can easily be determined by the color change (intense red to colorless) in the deprotonation. To a solution of chlorobis(ethylene)rhodium dimer (0.778 g, 2.0 mmol) in THF (10 mL) was added dropwise a suspension of (1,2,4-tri-*tert*-butylcyclopentadienyl)potassium at −40 °C. The solution was stirred at that temperature for 2 h and then warmed to 0 °C and evaporated. The residue was dissolved in diethyl ether, and the solution was filtered through a pad of alumina (3 × 2.2 cm) in diethyl ether. The solvent was evaporated and the residue crystallized from acetone at −78 °C. The product was obtained as yellow crystals (1.19 g, 75.9%). ^{1}H NMR (C_6D_6): δ 4.72 (s, 2H); 3.08−2.93 (m, 4H; complexed ethylene); 1.30 (s, 18H); 1.26 (s, 9H); 1.19−1.05 (m, 4H; complexed ethylene). ^{13}C{^{1}H} NMR (C_6D_6): δ 116.5 (d, J_{Rh-C} = 4.9 Hz); 114.2 (d, J_{Rh-C} = 3.9 Hz); 85.6 (d, J_{Rh-C} = 4.1 Hz); 38.2 (d, J_{Rh-C} = 13.2 Hz); 34.3; 33.2; 33.1; 31.5. Anal. Calcd for $C_{23}H_{37}Rh$: C, 64.27; H, 9.50. Found: C, 64.38; H, 9.76.

[1,2,4-*i*Pr$_3$-3,5-Me$_2$CpRh(CO)]$_2$ (3). The mixture of **1** (0.19 g, 0.5 mmol) and *tert*-butyl vinyl ether (1.5 mL, Aldrich) was heated at 120 °C in a Kontes flask for 15 h. The color changed from yellow to deep ink blue. The solution was evaporated and the residue recrystallized from hexanes at −30 °C. Dark blue-violet crystals were obtained (0.07 g, 40.0%). ^{1}H NMR (C_6D_{12}): δ 2.65 (septet, 2H; J = 7.2 Hz); 2.19 (septet, 1H; J = 7.2 Hz); 1.96 (s, 6H); 1.14 (d, 6H; J = 7.2 Hz); 1.13 (d, 6H; J = 7.2 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 250.5 (t, J_{Rh-C} = 54.6 Hz); 113.7 (d, J_{Rh-C} = 6.7 Hz); 112.3 (d, J_{Rh-C} = 7.8 Hz); 100.6 (d, J_{Rh-C} = 4.9 Hz); 25.7; 25.6; 24.4; 23.6; 22.9; 9.8 (d, J_{Rh-C} = 2.8 Hz). IR (solution in C_6D_{12}): ν_{CO} 1746 cm^{-1}. Anal. Calcd for $C_{34}H_{54}Rh_2O_2$: C, 58.29; H, 7.77. Found: C, 58.42; H, 7.94.

[1,2,4-*t*Bu$_3$CpRh(CO)]$_2$ (4). A mixture of **2** (0.15 g, 0.38 mmol), *tert*-butyl vinyl ether (0.20 mL, 1.52 mmol, Aldrich), and hexanes (5 mL) was heated in a Kontes flask for 8 h. The color changed from yellow to dark ink blue. The solvent was removed under vacuum and the residue heated (120 °C) under vacuum for 2 h followed by recrystallization from hexanes at −30 °C. Dark blue-violet crystals were obtained (0.05 g, 35.9%). ^{1}H NMR (C_6D_{12}): δ 4.97 (s, 1H); 1.31 (s, 18H); 0.97 (s, 9H). ^{13}C{^{1}H} NMR (C_6D_6): δ 245.7 (t, J_{Rh-C} = 54.5 Hz); 119.4 (d, J_{Rh-C} = 5.9 Hz); 115.9 (d, J_{Rh-C} = 8.3 Hz); 94.5; 34.0; 33.1; 31.2; 30.5. IR (solution in C_6D_{12}): ν_{CO} 1754 cm^{-1}. Anal. Calcd for $C_{36}H_{58}Rh_2O_2$: C, 59.34; H, 8.02. Found: C, 59.60; H, 8.18. The major byproduct observed was 1,2,4-*t*Bu$_3$CpRh(CO)$_2$ (comparison of crude reaction mixture NMR with an authentic sample).

1,2,4-*t*Bu$_3$CpRh(CO)$_2$ (5). (1,2,4-Tri-*tert*-butylcyclopentadienyl)potassium was prepared as in the case of **2** from 1,2,4-tri-*tert*-butylcyclopentadiene (0.385 g, 1.65 mmol) and benzylpotassium (0.230 g, 1.7 mmol) in THF (15 mL) at 0 °C. The suspension of the potassium salt was added dropwise to the suspension of chlorodicarbonylrhodium dimer (0.32 g, 0.82 mmol, Strem) in THF (5 mL) at −78 °C. The solution was stirred for 10 min at −78 °C and then warmed to room temperature and stirred for 30 min. The color of the mixture at this point was dark brown. The solvent was evaporated, the residue was dissolved in pentane, and this solution was filtered through Celite. After evaporation and crystallization from acetone at −78 °C a yellow solid that liquefies at room temperature was obtained; yield 0.52 g (80.8%). ^{1}H NMR (C_6D_{12}): δ 5.28 (s, 1H); 1.36 (s, 18H); 1.16 (s, 9H). ^{13}C{^{1}H} NMR (C_6D_{12}): δ 194.0 (d, J_{Rh-C} = 83.0 Hz); 119.7 (d, J_{Rh-C} = 4.3 Hz); 119.1 (d, J_{Rh-C} = 3.9 Hz); 85.8 (d, J_{Rh-C} = 3.5 Hz); 34.9; 32.5; 32.4; 30.6. IR (solution in C_6D_{12}): ν_{CO} 2032, 1968 cm^{-1}. Anal. Calcd for $C_{19}H_{29}RhO_2$: C, 58.16; H, 7.45. Found: C, 58.84; H, 7.60. The compound slowly decomposes under vacuum, producing **4**.

1,2,4-*t*Bu$_3$CpRh(CO)(C$_2$H$_4$) (7). Complex **2** (0.30 g, 0.77 mmol) was dissolved in toluene (20 mL), and CO was slowly bubbled through the solution for 6 h at 75 °C and then for 29 h at 70 °C. The yellow solution was evaporated (Schlenk flask kept at 0 °C at the end). Assay by ^{1}H NMR showed that the reaction mixture at that point contained 6% **5**, 7% **2**, and 87% **7**. The residue was recrystallized from acetone at −30 °C. A yellow powder that liquefies at room temperature was obtained; yield 0.22 g (73%). This material was contaminated with a few percent of **5** and **7**. The compound is stable at 0 °C under an inert temperature; however, in solution or neat at room temperature it decomposes to **4**. ^{1}H NMR (C_6D_{12}): δ 5.04 (s, 2H); 2.86 (br s, 2H); 2.27 (br s, 2H); 1.39 (s, 18H); 1.17 (s, 9H). ^{13}C{^{1}H} NMR (C_6D_{12}) δ 192.3 (d, J_{Rh-C} = 84.3 Hz); 118.6 (d, J_{Rh-C} = 4.3 Hz); 117.1 (d, J_{Rh-C} = 4.1 Hz); 85.3 (d, J_{Rh-C} = 3.6 Hz); 34.7; 32.9; 32.3; 31.5 (d, J_{Rh-C} = 12.9 Hz); 31.2. IR (solution in C_6D_{12}): ν_{CO} 1972 cm^{-1}. Anal. Calcd for $C_{20}H_{33}RhO$: C, 61.22; H, 8.48. Found: C, 61.32; H, 8.53.

General Procedure for the NMR-Scale Decarbonylation of Ketones. In the glovebox, a Teflon-stoppered NMR tube (J. Young) was charged with the rhodium complex **2** (0.05 mmol, 0.0196 g), ketone (0.2 mmol), a capillary insert containing a mixture of tetrachloroethane and tetrachloroethane-d_2 (external standard for NMR, 5.20 ppm), and cyclohexane-d_{12} (0.5 mL, Cambridge Isotope Laboratories). After the NMR spectrum is recorded, the mixture was heated at 120 °C with periodic monitoring of the conversion by NMR spectroscopy (integration of [1,2,4-*t*Bu$_3$CpRh(CO)]$_2$ resonances at 4.97, 1.31, and 0.97 ppm and 1,2,4-*t*Bu$_3$CpRh(CO)(ethylene) resonances at 5.03, 1.38, and 1.16 ppm vs the capillary standard). Some unidentified 1,2,4-*t*Bu$_3$Cp-containing species were observed in the reaction mixtures during the reaction. Occasionally the reaction mixtures were separated on silica gel to compare the spectra of products with the spectra of authentic samples purchased from commercial suppliers.

Decarbonylation of 3,5,3′,5′-Tetrakis(trifluoromethyl)-benzophenone (10a). The NMR spectra were recorded at 70 °C due to the insolubility of 3,5,3′,5′-tetrakis(trifluoromethyl)-benzophenone (Lancaster) in the reaction mixture at room temperature. At initial stages of the reaction the ketone was not completely soluble in C_6D_{12}, even at 120 °C.

The following data points were acquired (time, conversion to 1,2,4-*t*Bu$_3$CpRh(CO)(C$_2$H$_4$), conversion to [1,2,4-*t*Bu$_3$CpRh-(CO)]$_2$ with respect to 1,2,4-*t*Bu$_3$CpRh(C$_2$H$_4$)$_2$): 3 h, 19%, 9%; 7 h, 22%, 28%; 9 h, 30%, 36%; 13 h, 21%, 53%; 26 h, ND, 68%.

After the thermolysis the reaction mixture was chromatographed (silica gel) in hexanes to elute 3,5,3′,5′-tetrakis-(trifluoromethyl)biphenyl (^{1}H NMR spectrum compared with an authentic sample purchased from Maybridge) followed by 2/1 hexanes/toluene to elute a mixture of unreacted 3,5,3′,5′-tetrakis(trifluoromethyl)benzophenone and [1,2,4-*t*Bu$_3$CpRh-(CO)]$_2$. R_f(3,5,3′,5′-tetrakis(trifluoromethyl)biphenyl, hexanes) = 0.36. R_f(3,5,3′,5′-tetrakis(trifluoromethyl)benzophenone, 2/1 hexanes/toluene) = 0.53. R_f([1,2,4-*t*Bu$_3$CpRh(CO)]$_2$, 2/1 hexanes/toluene) = 0.43. No ortho-ethylation product (or any other organic product besides biphenyl and unreacted benzophenone) was observed.

Decarbonylation of 3,3′-Bis(trifluoromethyl)benzophenone (10b). The ketone was purchased from Aldrich. The following data points were acquired (time, conversion to 1,2,4-*t*Bu$_3$CpRh(CO)(C$_2$H$_4$), conversion to [1,2,4-*t*-Bu$_3$CpRh(CO)]$_2$ with respect to 1,2,4-*t*Bu$_3$CpRh(C$_2$H$_4$)$_2$, conversion to 2-ethyl-5,3′-bis(trifluoromethyl)benzophenone with respect to 3,3′-bis-(trifluoromethyl)benzophenone: 1 h, 31%, 14%, 25%; 2 h, 36%, 41%, 35%; 3 h, 25%, 48%, no further change in the amount of ethylated benzophenone; 4.5 h, 20%, 58%; 6.5 h, 18%, 69%; 10.5 h, 11%, 74%.

After the thermolysis the reaction mixture was chromatographed (silica gel) in hexanes to elute 3,3′-bis(trifluoromethyl)biphenyl (^{1}H NMR shifts compared with literature values)[25] followed by 5/1 hexanes/dichloromethane to elute a mixture

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of 2-ethyl-5,3′-bis(trifluoromethyl)benzophenone and [1,2,4-*t*Bu$_3$CpRh(CO)]$_2$. After that, unreacted 3,3′-bis(trifluoromethyl)benzophenone was eluted. R_f(3,3′-bis(trifluoromethyl)-biphenyl, hexanes) = 0.39. R_f(2-ethyl-5,3′-bis(trifluoromethyl)-benzophenone, 4/1 hexanes/dichloromethane) = 0.28. R_f([1,2,4-*t*-Bu$_3$CpRh(CO)]$_2$, 4/1 hexanes/dichloromethane) = 0.35. R_f-(3,3′-bis(trifluoromethyl)benzophenone, 4/1 hexanes/dichloromethane) = 0.19.

Decarbonylation of Benzophenone (10c). The ketone was purchased from Aldrich. The following data points were acquired (time, conversion to 1,2,4-*t*Bu$_3$CpRh(CO)(C$_2$H$_4$), conversion to [1,2,4-*t*Bu$_3$CpRh(CO)]$_2$ with respect to 1,2,4-*t*Bu$_3$-CpRh(C$_2$H$_4$)$_2$, conversion to the known 2-ethylbenzophenone[26] with respect to benzophenone: 1 h, 23%, 15%, 30%; 2 h, 19%, 25%, 38%; 3 h, 15%, 42%, no further change in the amount of ethylated benzophenone; 4.5 h, 11%, 46%; 6.5 h, 8%, 50%; 10.5 h, <5%, 61%.

Decarbonylation of 4,4′-Dimethylbenzophenone (10d). The ketone was purchased from Aldrich. The following data points were acquired (time, conversion to 1,2,4-*t*Bu$_3$CpRh(CO)-(C$_2$H$_4$), conversion to [1,2,4-*t*Bu$_3$CpRh(CO)]$_2$ with respect to 1,2,4-*t*Bu$_3$CpRh(C$_2$H$_4$)$_2$, conversion to 2-ethyl-4,4′-dimethylbenzophenone with respect to 4,4′-dimethylbenzophenone: 1 h, 20%, 16%, 28%; 2 h, 13%, 29%, 37%; 3 h, 11%, 33%, no further change in the amount of ethylated benzophenone; 4.5 h, 9%, 35%; 6.5 h, 7%, 40%; 10.5 h, 5%, 50%.

Decarbonylation of 4-(Trifluoromethyl)acetophenone (10e). The ketone was purchased from Aldrich. The following data points were acquired (time, conversion to 1,2,4-*t*Bu$_3$CpRh-(CO)(C$_2$H$_4$), conversion to [1,2,4-*t*Bu$_3$CpRh(CO)]$_2$ with respect to 1,2,4-*t*Bu$_3$CpRh(C$_2$H$_4$)$_2$, conversion to the mixture of 2-ethyl-4-(trifluoromethyl)acetophenone and 2,6-diethyl-4-(trifluoromethyl)acetophenone with respect to 4-(trifluoromethyl)-acetophenone: 1 h, <2%, <2%, 6%; 4 h, 11%, 4%, 16%; 7 h, 11%, 11%, 20%; 11 h, 10%, 20%, 25%; 15 h, 7%, 23%, 27%; 23 h, 4%, 30%, no further change in the amount of ethylated acetophenones; 36 h, <2%, 34%.

After thermolysis the reaction mixture was chromatographed (silica gel) in hexanes followed by 4/1 hexanes/toluene and then 3/1 hexanes/toluene. [1,2,4-*t*Bu$_3$CpRh(CO)]$_2$ was eluted, followed by a mixture of the known 2-ethyl-4-(trifluoromethyl)acetophenone and 2,6-diethyl-4-(trifluoromethyl)-acetophenone.[27] After that 4-(trifluoromethyl)acetophenone was eluted. R_f(hexanes) = 0.39. R_f(2-ethyl-4-(trifluoromethyl)-acetophenone and 2,6-diethyl-4-(trifluoromethyl)acetophenone, 4/1 hexanes/toluene) = 0.20. R_f([1,2,4-*t*Bu$_3$CpRh(CO)]$_2$, 4/1 hexanes/toluene) = 0.38. R_f(4-(trifluoromethyl)acetophenone, 4/1 hexanes/toluene) = 0.13. 4-(Trifluoromethyl)toluene was not isolated due to volatility; it was observed in the crude reaction mixture by NMR.

Decarbonylation of Acetophenone (10f). The ketone was purchased from Aldrich. The following data points were acquired (time, conversion to 1,2,4-*t*Bu$_3$CpRh(CO)(C$_2$H$_4$), conversion to [1,2,4-*t*Bu$_3$CpRh(CO)]$_2$ with respect to 1,2,4-*t*Bu$_3$-CpRh(C$_2$H$_4$)$_2$, conversion to 2-ethylacetophenone[28] with respect to acetophenone: 1 h, <2%, <2%, <2%; 4 h, <2%, <2%, <10%; 7 h, 7%, <2%, <10%; 11 h, 9%, 4%, ND; 15 h, 7%, 9%, ND; 23 h, 5%, 17%, ND; 36 h, <2%, 24%, 18%.

Decarbonylation of *β*-Phenylpropiophenone: Preparation of the Chalcone Adduct 13. In the glovebox a Teflon-stoppered NMR tube (J. Young) was charged with the rhodium complex **2** (0.097 g, 0.25 mmol), *β*-phenylpropiophenone (0.052 g, 0.25 mmol, Lancaster), and cyclohexane-d_{12} (0.5 mL, Cambridge Isotopes). The mixture was thermolyzed at 120 °C for 35 h. At that point the mixture was red-brown and an incomplete conversion (ca. 50%) to intermediate **13** was observed. The mixture was then heated at 150 °C for 18 h. The color changed to greenish blue, and the formation of [1,2,4-*t*Bu$_3$CpRh(CO)]$_2$ (ca. 70% conversion) was observed by ^{1}H NMR. After that, the mixture was chromatographed on silica gel with hexanes as eluent. After a trace of unreacted **2** and **7**, stilbene (0.016 g) was eluted, contaminated with <5% of bibenzyl. The column was dried out, and the residual mixture was left on the silica gel for 1 day to decompose the rhodium complexes. After that, elution with toluene/hexane (1/2) afforded a mixture of starting ketone with unidentified impurities followed by impure chalcone (0.027 g). The ^{1}H NMR spectra of chalcone and stilbene were compared with the spectra of commercial materials (Aldrich). R_f(stilbene, hexanes) = 0.34. R_f(chalcone, 1/1 hexanes/toluene) = 0.15.

A mixture of chalcone (0.108 g, 0.52 mmol, Aldrich) and 1,2,4-*t*Bu$_3$CpRh(C$_2$H$_4$)$_2$ (0.20 g, 0.52 mmol) was heated in hexanes (1 mL) for 18 h at 120 °C. At this point assay by ^{1}H NMR showed >95% conversion to the product, which was identical with the product obtained by the thermolysis of *β*-phenylpropiophenone and 1,2,4-*t*Bu$_3$CpRh(C$_2$H$_4$)$_2$ at 120 °C. The reaction mixture was evaporated and the residue twice recrystallized from acetone at −30 °C to afford 0.188 g (66.4%) of rust-colored crystals. The structure was verified by X-ray crystallography. ^{1}H NMR (C$_6$D$_{12}$): 7.99−7.87 (m, 2H); 7.36−7.19 (m, 5H); 7.14−7.04 (m, 2H); 7.02−6.92 (m, 1H); 5.95 (dd, 1H; J_1 = 8.3 Hz, J_2 = 0.8 Hz); 4.25 (d, J = 1.9 Hz); 3.85 (d, J = 1.9 Hz); 3.4 (d, J = 8.3 Hz); 1.41 (s, 9H); 1.17 (s, 9H); 0.89 (s, 9H). ^{13}C{^{1}H} NMR (C$_6$D$_{12}$): 144.9; 139.1; 130.5 (d, J_{Rh-C} = 5.9 Hz; C=O); 129.6; 128.5; 128.1; 127.1; 125.5; 116.1 (d, J_{Rh-C} = 6.1 Hz); 114.1 (d, J_{Rh-C} = 7.4 Hz); 110.8 (d, J_{Rh-C} = 7.9 Hz); 81.7 (d, J_{Rh-C} = 5.4 Hz); 77.8 (d, J_{Rh-C} = 8.7 Hz); 71.9 (d, J_{Rh-C} = 6.6 Hz); 61.0 (d, J_{Rh-C} = 13.9 Hz); 34.1; 33.5; 33.3; 32.5; 31.4; 30.8. The signal of one aromatic carbon could not be located. Anal. Calcd for C$_{32}$H$_{41}$RhO: C, 70.58; H, 7.59. Found: C, 70.41; H, 7.65.

Preparative-Scale Decarbonylation of 4,4′-Dimethylbenzophenone (10d). In the glovebox a Teflon-stoppered NMR tube (J. Young) was charged with the rhodium complex **2** (0.059 g, 0.15 mmol), 4,4′-dimethylbenzophenone (0.106 g, 0.50 mmol, Aldrich), and cyclohexane-d_{12} (0.5 mL) and heated at 120 °C for 17 h. The reaction mixture was purified by chromatography in hexanes as eluent to give 4,4′-dimethylbiphenyl (0.017 g, 62% based on **2**). The elution was continued using 3/1 hexanes/toluene to give [1,2,4-*t*Bu$_3$CpRh(CO)]$_2$ (0.02 g, 37%). After that, elution was continued with 1/1 hexanes/toluene to give 2-ethyl-4,4′-dimethylbenzophenone (0.047 g, 66%) and unreacted 4,4′-dimethylbenzophenone (0.029 g, 27%). The ^{1}H NMR spectrum of 4,4′-dimethylbiphenyl was compared with the spectrum of the commercial material (Aldrich). R_f-(4,4′-dimethylbiphenyl, hexanes) = 0.28. R_f(2-ethyl-4,4′-dimethylbenzophenone, toluene) = 0.39. R_f(4,4′-dimethylbenzophenone, toluene) = 0.31.

Characterization data for 2-ethyl-4,4′-dimethylbenzophenone are as follows. ^{1}H NMR (CDCl$_3$): δ 7.72−7.66 (m, 2H); 7.24−7.20 (m, 2H); 7.16 (d, 1H; J = 7.7 Hz); 7.13 (s, 1H); 7.02 (d, 1H; J = 7.7 Hz); 2.64 (q, 2H; J = 7.5 Hz); 2.40 (s, 3H); 2.38 (s, 3H); 1.14 (t, 3H; J = 7.5 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 198.4; 143.8; 143.2; 140.2; 135.8; 135.7; 130.3; 130.2; 129.0; 128.7; 125.7; 26.4; 21.6; 21.4; 16.0. Anal. Calcd for C$_{17}$H$_{18}$O: C, 85.67; H, 7.61. Found: C, 85.13; H, 7.62.

Preparative-Scale Decarbonylation of 3,3′-Bis(trifluoromethyl)benzophenone (10b). In the glovebox a Kontes flask was charged with the rhodium complex **2** (0.098 g, 0.25 mmol), 3,3′-bis(trifluoromethyl)benzophenone (0.318 g, 1.0 mmol, Aldrich), and toluene (3 mL). The reaction mixture was heated at 135 °C for 23 h. Crude NMR showed the presence of only **10b**, **11b**, **12b**, **4**, and **7** in the reaction mixture at that point. The reaction mixture was purified by chromatography in hexanes, eluting 3,3′-bis(trifluoromethyl)biphenyl contaminated with **7** (0.07 g of impure material, contained 0.06 g of biphenyl (82.2%) and 0.01 g of **7**). The elution was continued

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Table 2. Crystallographic Data Collection Parameters for 1 and 13

	1	13
formula	$C_{20}H_{35}Rh$	$C_{32}H_{41}RhO$
mol wt	370.4	544.6
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$	$Fdd2$
a, Å	9.0105(3)	31.3052(7)
b, Å	16.5882(6)	39.2724(9)
c, Å	12.8672(4)	8.9197(2)
β, deg	95.933(1)	
V, Å^3	1912.93(11)	10966.1(4)
Z	4	16
calcd density, Mg/m^3	1.314	1.319
F(000)	795.83	4560.13
cryst dimens, mm	0.25 × 0.25 × 0.10	0.30 × 0.10 × 0.10
temp, °C	−100	−100
radiation (λ), Å	0.710 73	0.710 73
$2\theta_{max}$, deg	65.0	56.0
μ, mm^{-1}	0.89	0.64
total no. of rflns	35 313	42 823
total no. of unique rflns	6953	6529
no. of obsd data ($I > 2.5\sigma(I)$)	5741	5499
no. of refined params	331	306
R_F, %	0.034	0.033
R_w, %	0.042	0.032
GOF	1.7561	1.1250

using 6/1 hexanes/dichloromethane to give a mixture of [1,2,4-*t*Bu$_3$CpRh(CO)]$_2$ and 2-ethyl-5,3′-bis(trifluoromethyl)benzophenone. After that, impure 3,3′-bis(trifluoromethyl)benzophenone (0.142 g) was eluted. The ^{1}H NMR shift values of 3,3′-bis(trifluoromethyl)biphenyl were compared with the literature values.[25] The fraction containing the ethylated benzophenone was adsorbed on silica gel and kept for 24 h to decompose the rhodium complex. Elution with 6/1 hexanes/dichloromethane afforded 2-ethyl-5,3′-bis(trifluoromethyl)benzophenone (0.103 g) contaminated with <5% of an impurity (most likely 2,2′-diethyl-5,5′-bis(trifluoromethyl)benzophenone).

Characterization data for 2-ethyl-5,3′-bis(trifluoromethyl)-benzophenone are as follows. ^{1}H NMR ($CDCl_3$): δ 8.1 (s, 1H); 7.90 (d, 1H; J = 7.8 Hz); 7.86 (d, 1H; J = 7.8 Hz); 7.70 (d, 1H; J = 8.0 Hz); 7.61 (t, 1H; J = 7.8 Hz); 7.51 (s, 1H); 7.50 (d, 1H; J = 8.0 Hz); 2.70 (q, 2H; J = 7.6 Hz); 1.18 (t, 3H; J = 7.6 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 195.6; 147.3; 138.0; 137.7; 133.3; 131.6 (q, J_{C-F} = 33.1 Hz); 130.3; 130.1 (q, J_{C-F} = 3.4 Hz); 129.4; 128.2 (q, J_{C-F} = 33.0 Hz); 127.4 (q, J_{C-F} = 3.6 Hz); 126.6 (q, J_{C-F} = 3.8 Hz); 125.0 (q, J_{C-F} = 3.8 Hz); 123.8 (q, J_{C-F} = 272.3 Hz); 123.5 (q, J_{C-F} = 272.7 Hz); 26.4; 15.5. Anal. Calcd for $C_{17}H_{12}F_6O$: C, 58.97; H, 3.49. Found: C, 59.25; H, 3.63.

X-ray Crystal Structures (1, 13). Diffraction data were collected on a Bruker SMART 1K diffractometer using the ω-scan mode. Refinement was carried out with the full-matrix least-squares method based on F (NCRVAX) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. Complete details of X-ray data collection are given in Table 2.

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Supporting Information Available: Tables giving X-ray crystallographic data for **1** and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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