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Cyclobutadiene Arene Complexes of Rhodium and Iridium

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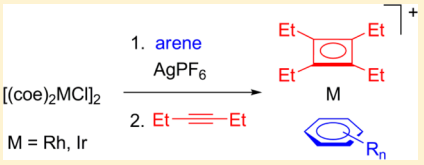
Supporting Information

ABSTRACT: Reactions of $[(C_2H_4)_2RhCl]_2$ or $[(coe)_2RhCl]_2$ (coe = cyclooctene) with $AgPF_6$ and arenes, followed by addition of 3-hexyne, give the cyclobutadiene complexes $[(C_4Et_4)Rh(arene)]^+$ in 40−65% yield (arene = *tert*-butylbenzene, *p*-xylene, mesitylene, 4-mesitylbutanoic acid). In the absence of arenes, the hexaethylbenzene complex $[(C_4Et_4)Rh(C_6Et_6)]^+$ is formed in 70% yield as a result of cyclotrimerization of 3-hexyne in the coordination sphere of rhodium. Similar reaction of $[(coe)_2IrCl]_2$ with $AgPF_6$ and 3-hexyne leads to $[(C_4Et_4)Ir(C_6Et_6)]^+$, which is apparently the first reported cyclobutadiene iridium complex. DFT calculations suggest that formation of the model cyclobutadiene complex $[(C_4Me_4)Rh(C_6H_6)]^+$ from bis(alkyne) intermediate $[(C_2Me_2)_2Rh(C_6H_6)]^+$ can proceed via a metallacycle transition state with a low energy barrier of 14.5 kcal mol^{-1}.



INTRODUCTION

Metallocenes Cp_2M are one of the major classes of organometallic compounds with potential for application in many areas.[1,2] Compared to metallocenes, the isoelectronic sandwich complexes (cyclobutadiene)M(arene), so-called isometallocenes,[3] have been very briefly studied. As far as we aware, only a few complexes of this type have been reported, namely, $(C_4Ph_4)Fe(toluene)$,[4] $[(C_4R_4)Co(arene)]^+$,[3,5] and $[(C_4Me_4)M(C_6Me_6)]^{2+}$ (M = Ni, Pt).[6,7] Among them the cobalt complex $[(C_4Me_4)Co(C_6H_6)]^+$ has attracted the most attention, because it readily exchanges benzene for other ligands and therefore represents a convenient precursor for various $(C_4Me_4)Co$ compounds.[8] Recently we have described the synthesis and catalytic application of the first rhodium isometallocenes $[(C_4R_4)Rh(p\text{-xylene})]^+$.[9,10] Herein we report the preparation of $[(C_4Et_4)Rh(arene)]^+$ complexes with various arene ligands as well as the synthesis of the first iridium cyclobutadiene complex, $[(C_4Et_4)Ir(C_6Et_6)]^+$.

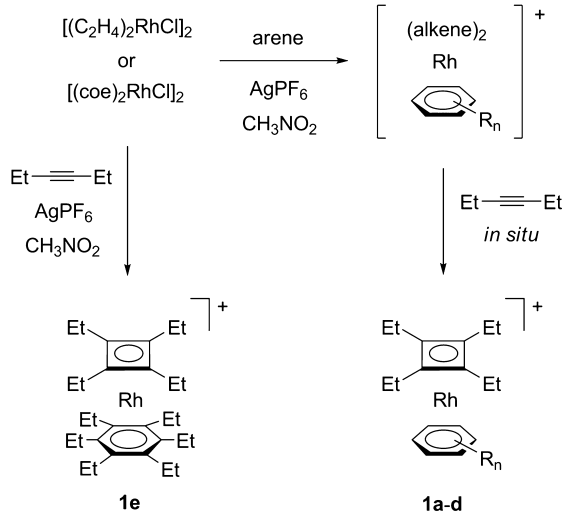
RESULTS AND DISCUSSION

Cation $[(C_4Et_4)Rh(p\text{-xylene})]^+$ (**1a**) was prepared by a *one-pot* procedure from the commercially available ethylene complex $[(C_2H_4)_2RhCl]_2$ (Scheme 1).[9] First, the reaction of $[(C_2H_4)_2RhCl]_2$ with *p*-xylene and $AgPF_6$ in nitromethane produced the intermediate $[(C_2H_4)_2Rh(p\text{-xylene})]^+$. The addition of 3-hexyne led to replacement of ethylene ligands and formation of the cyclobutadiene complex **1a**, which was isolated in ca. 50% overall yield.

Further investigation showed that this procedure is also suitable for the synthesis of complexes $[(C_4Et_4)Rh(arene)]^+$ (**1b,c**) with other alkylbenzenes, such as *tert*-butylbenzene and mesitylene. A similar reaction with hexamethylbenzene stopped at the first stage to give the intermediate ethylene complex $[(C_2H_4)_2Rh(C_6Me_6)]^+$ (**2**, 84% yield), presumably because of the steric hindrance of the C_6Me_6 ligand. Heating of **2** with 3-hexyne at 80 °C gave only traces of the corresponding cyclobutadiene complex $[(C_4Et_4)Rh(C_6Me_6)]^+$.

In contrast to alkylbenzenes, functionally substituted arenes, such as 1,4-dimethoxybenzene, 2-mesitylacetonitrile, ethyl ester of *N*-acetylphenylalanine, and thiophene, did not give cyclobutadiene rhodium complexes under similar conditions. Apparently, the $[(C_2H_4)_2Rh]^+$ fragment coordinates with heteroatoms of these arenes and in this way alters further

Scheme 1. Synthesis of Cyclobutadiene Rhodium Complexes



arene = p-xylene (**a**), tert-butylbenzene (**b**), mesitylene (**c**), 4-mesityl-butanoic acid (**d**)

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reaction with alkyne. The only exception was 4-mesitylbutanoic acid, which produced the corresponding complex **1d** in 48% yield.

Interestingly, the reaction of $[(C_2H_4)_2RhCl]_2$ with $AgPF_6$ and 3-hexyne in the absence of any arene gave hexaethylbenzene complex $[(C_4Et_4)Rh(C_6Et_6)]^+$ (**1e**; 35% yield) as a result of cyclotrimerization of 3-hexyne in the coordination sphere of rhodium.[11] This complex was also obtained in the presence of weakly coordinating arenes, such as naphthalene. In the case of benzene, the reaction produced a mixture of cationic complexes $[(C_4Et_4)Rh(C_6H_6)]^+$ and **1e** in 3:1 ratio.

In order to improve the synthesis of the representative complex **1a**, we used the cyclooctene precursor $[(coe)_2RhCl]_2$ (coe = cyclooctene) as a starting material instead of $[(C_2H_4)_2RhCl]_2$. Following the general procedure $[(coe)_2RhCl]_2$ was converted into **1a** in a better yield of 65%. Replacement of the cyclooctene ligands in the intermediate cation $[(coe)_2Rh(p\text{-xylene})]^+$ (**3**; Figure 1) is a bit slower compared to replacement of ethylene in $[(C_2H_4)_2Rh(p\text{-xylene})]^+$, and therefore reaction with 3-hexyne was carried out at 60 °C to ensure complete conversion. In the absence of arenes heating of $[(coe)_2RhCl]_2$ with $AgPF_6$ and 3-hexyne produced hexaethylbenzene complex **1e** in a good yield of 70%.

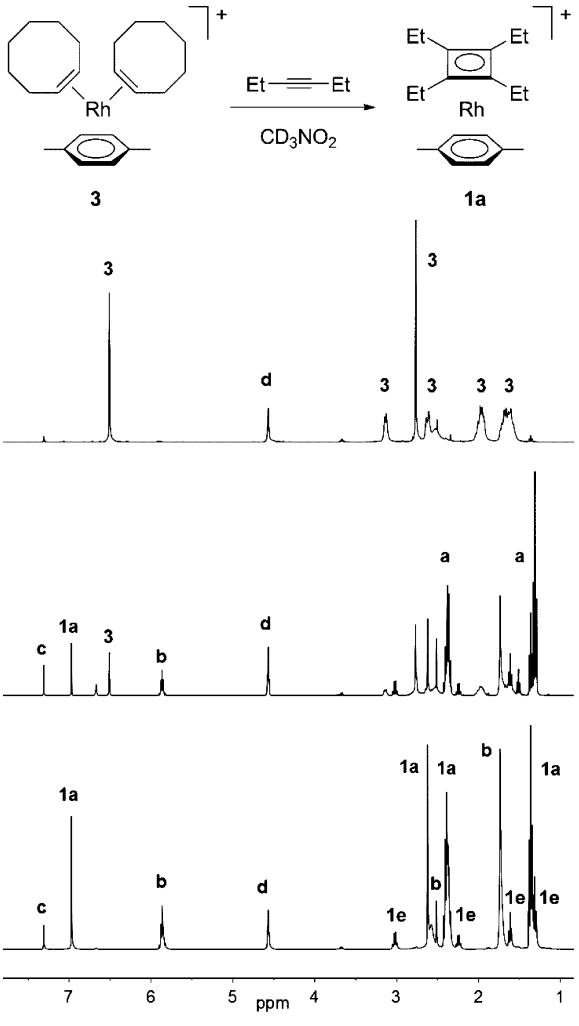
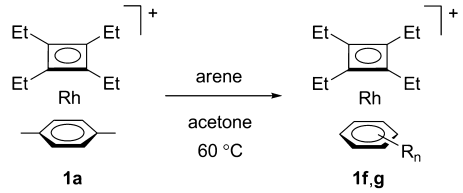


Figure 1. ^1H NMR spectra of reaction of **3** with 3-hexyne in CD_3NO_2 at 25 °C. Top: Before addition of 3-hexyne; center: 3 h after addition; bottom: 14 h after addition (full conversion into **1a** and **1e**). Signal assignment: **a**, 3-hexyne; **b**, free cyclooctene; **c**, free xylene; **d**, CHD_2NO_2 (residual solvent signal).

We have monitored the reaction of the cyclooctene complex **3** with 3-hexyne at 25 °C by ^1H NMR (Figure 1) and observed clean formation of the target cyclobutadiene complex **1a** along with small amounts of the byproduct **1e** (less than 10%). In preparative experiments this byproduct was easily removed during reaction workup because it has higher solubility and does not precipitate with the target product **1a**. No distinct intermediates were detected by ^1H NMR monitoring. This suggests that replacement of the first cyclooctene ligand in **3** is a rate-determining step of the whole process. The substitution probably proceeds via an associative mechanism; dissociative substitution is unlikely because it would require heating above 100 °C, as in the case of the related complex $CpRh(C_2H_4)_2$.[12]

In order to prepare rhodium complexes with functionally substituted arenes, we studied the ligand exchange in the cation **1a** (Scheme 2). It was found that heating of **1a** with

Scheme 2. Arene Exchange in the Rhodium Complex 1a

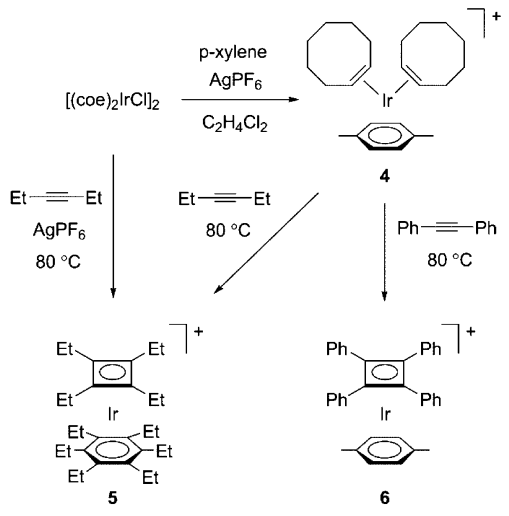


arene = 4-methylaniline (**f**), 2-mesityl-acetonitrile (**g**)

4-methylaniline or 2-mesitylacetonitrile at 60 °C in acetone cleanly gives the corresponding complexes **1f,g**. On the other hand similar reactions did not proceed in the case of less donating arenes such as 1,4-dimethoxybenzene, ethyl ester of *N*-acetylphenylalanine, and thiophene. It is interesting to note that the $[(C_4Et_4)Rh]^+$ fragment prefers η^6-coordination with 4-methylaniline in contrast to the related $[(nbd)Rh]^+$ fragment, which forms a complex with N-coordinated aniline $[(nbd)Rh(C_6H_5NH_2)_2]^+$.[13]

Finally, we tried to synthesize cyclobutadiene iridium complexes using our general approach. Treatment of $[(coe)_2IrCl]_2$ with $AgPF_6$ and *p*-xylene gave the expected complex $[(coe)_2Ir(p\text{-xylene})]^+$ (**4**) in 64% yield (Scheme 3).

Scheme 3. Synthesis of Cyclobutadiene Iridium Complexes



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However, its further reaction with 3-hexyne under various conditions produced only the hexaethylbenzene complex $[(C_4Et_4)Ir(C_6Et_6)]^+$ (**5**). The displacement of *p*-xylene in **4** by 3-hexyne is in accordance with the known lability of the iridium–arene bond.[14] Compound **5** was also obtained in 65% yield by the direct reaction of $[(coe)_2IrCl]_2$ with 3-hexyne and $AgPF_6$. The reaction of $[(coe)_2Ir(p\text{-xylene})]^+$ (**4**) with diphenylacetylene apparently gave the cyclobutadiene complex $[(C_4Ph_4)Ir(p\text{-xylene})]^+$ (**6**). However, this compound slowly decomposed into insoluble unidentified products, so we managed to characterize it only by ^1H and ^{13}C NMR spectra. To the best of our knowledge, **5** and **6** are the only cyclobutadiene iridium complexes reported to date.

All cationic complexes were isolated as air-stable salts with PF_6^- anions (in some cases also with BF_4^- or OTf^- anions). They were characterized by ^1H and ^{13}C NMR spectroscopy as well as by elemental analysis. Hexaethylbenzene complexes of rhodium [**1e**]PF_6 and iridium [**5**]PF_6 form good crystals, in which, however, the cations are strongly disordered. On the other hand, we managed to establish the structures of [**1d**]BF_4 (Figure 2) and [**2**]PF_2O_2 (Figure 3) by the X-ray diffraction

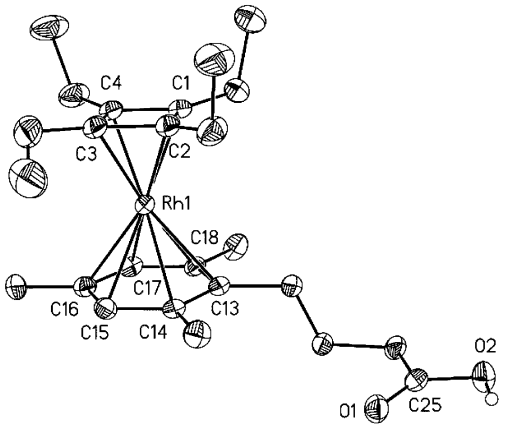

Figure 2. Crystal structure of complex [**1d**]BF_4 in 50% thermal ellipsoids. Counterion, disordered fragment of one of the ethyl groups, and all hydrogen atoms (except that of the COOH group) are omitted for clarity. Selected interatomic distances (Å): Rh1–C1 2.097(3), Rh1–C2 2.101(3), Rh1–C3 2.095(3), Rh1–C4 2.098(3), Rh1–C13 2.290(3), Rh1–C14 2.292(3), Rh1–C15 2.280(3), Rh1–C16 2.292(3), Rh1–C17 2.274(3), Rh1–C18 2.290(3), C1–C2 1.449(4), C2–C3 1.461(4), C3–C4 1.447(5), C1–C4 1.454(4), Rh···C_4(plane) 1.829, Rh···C_6(plane) 1.796.

analysis. The cyclobutadiene ligand in cation **1d** is a flat square with mean C–C distance of 1.453 Å, which is similar to that observed in complexes of other metals.[15] Interestingly, Rh···C_6(plane) distances are almost the same for bis(ethylene) and cyclobutadiene complexes **2** and **1d**.

We investigated the possible mechanism of formation of cyclobutadiene complexes from the model bis(alkyne) intermediate $[(C_2Me_2)_2Rh(C_6H_6)]^+$ (**7**) by DFT calculations (Figure 4). As expected,[16] the transition state for direct 2+2 dimerization of alkynes in **7** was not located because such a process is symmetry-forbidden. Instead, it was found that **7** can easily rearrange into more stable metallacycle **8** via transition state **TS1** with a free energy barrier of 14.5 kcal mol^{-1}. The metallacycle **8** further transforms into the cyclobutadiene complex **9** via low-lying nonsymmetrical transition state **TS2** (6.2 kcal mol^{-1} barrier). Overall the process is thermodynamically favorable for 47.6 kcal mol^{-1}. Low activation barriers correlate with reasonably fast reaction at room temperature. A generally similar mechanism with 14.6 and 19.4 kcal mol^{-1} barriers was proposed for conversion of the bis(acetylene) complex $CpRh(C_2H_2)_2$ into the cyclobutadiene complex $CpRh(C_4H_4)$.[16]

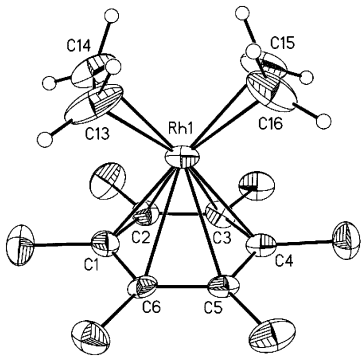

Figure 3. Crystal structure of complex [**2**]PF_2O_2 in 50% thermal ellipsoids. Counterion and the hydrogen atoms of C_6Me_6 ligand are omitted for clarity. Selected interatomic distances (Å): Rh1–C1 2.205(10), Rh1–C2 2.281(9), Rh1–C3 2.313(10), Rh1–C4 2.250(9), Rh1–C5 2.316(8), Rh1–C6 2.316(9), Rh1–C13 2.112(11), Rh1–C14 2.108(11), Rh1–C15 2.124(11), Rh1–C16 2.113(11), Rh···C_6(plane) 1.795.

Alternatively, the starting complex **7** can add one more alkyne molecule to give the tris(alkyne) complex $[(C_2Me_2)_3Rh(\eta^2\text{-}C_6H_6)]^+$ (**10**) with η^2-coordination of the benzene ligand. This process has a rather high free energy barrier of 18.7 kcal mol^{-1} (**TS3**) due to a negative entropy contribution. The barrier is expected to be lower for the weakly coordinating arenes such as naphthalene.[17] The intermediate **10** dissociates into $[(C_2Me_2)_3Rh]^+$ (**11**) and free benzene without traceable barrier. Apparently, the unsaturated complex **11** then coordinates with additional alkyne molecules, eventually giving fully substituted cyclobutadiene arene complex $[(C_4Me_4)Rh(C_6Me_6)]^+$ (**12**), an analogue of the experimentally observed $[(C_4Et_4)Rh(C_6Et_6)]^+$ (**1e**).

We also briefly investigated the catalytic activity of several rhodium complexes in the reductive amination reaction using carbon monoxide as reducing agent. It was found that both olefin (**2** and **3**) and cyclobutadiene (**1a** and **1f**) complexes (at 1 mol % loading) promote the conversion of *p*-methylbenzaldehyde and *p*-methoxyaniline into the benzylaniline **13** under low pressure of CO (Scheme 4). In all cases full conversion of the starting materials and 89–96% yield of the product **13** was observed. This contradicts our previous assumption[9b] that the cyclobutadiene ligand is crucial for effective stabilization of the catalytically active species. Further experiments on the catalytic activity of the olefin rhodium complexes are under way.

In summary, we have developed a one-step method for synthesis of the cyclobutadiene rhodium complexes $[(C_4Et_4)Rh(arene)]^+$ from the readily available precursors $[(C_2H_4)_2RhCl]_2$ and $[(coe)_2RhCl]_2$ and showed its limitations. The attempts to prepare similar iridium compounds led to the hexaethylbenzene complex $[(C_4Et_4)Ir(C_6Et_6)]^+$ as a result of cyclotrimerization of 3-hexyne in the coordination sphere of the metal. The DFT calculations suggested a mechanism for formation of the cyclobutadiene ligand from two alkynes via a metallacycle intermediate with a low activation barrier.

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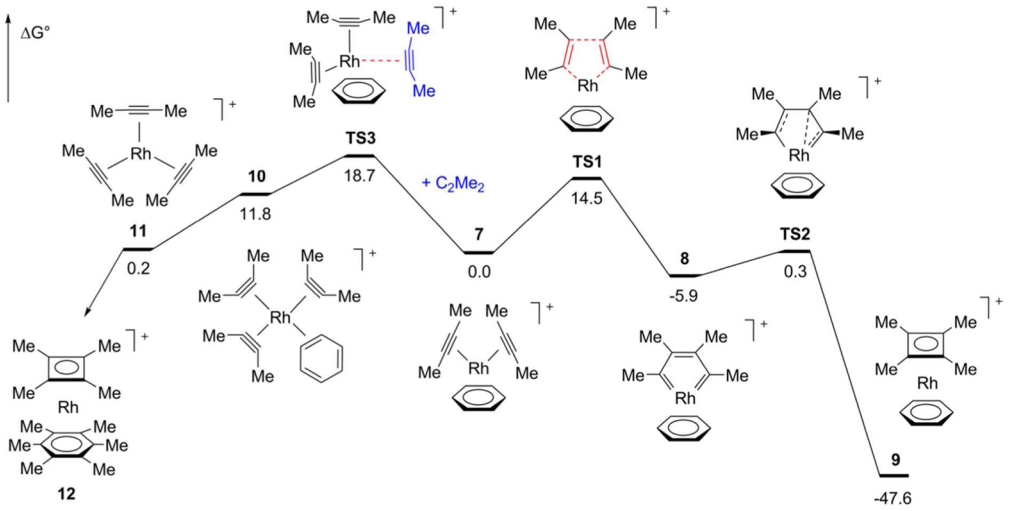
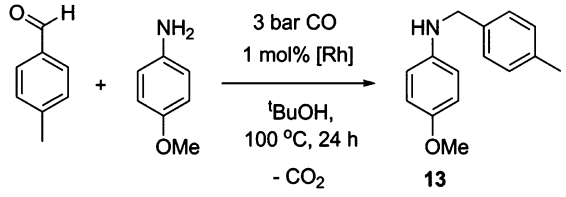


Figure 4. Calculated mechanism of formation of the cyclobutadiene complexes (at PBE/3z level). ΔG values are given in kcal mol^{-1} at 298 K relative to the starting bis(alkyne) complex 7.

Scheme 4. Reductive Amination under Rhodium Catalysis



EXPERIMENTAL SECTION

General Procedures. All reactions were carried out under an argon atmosphere in anhydrous solvents, which were purified and dried using standard procedures. Isolation of all products was carried out in air. ^{1}H and ^{13}C NMR spectra were measured with a Bruker Avance 400 spectrometer at 20 °C. Chemical shifts are reported in ppm using the residual signals of the solvents as internal standards. Complexes $[(C_2H_4)_2RhCl]_2$,[18] $[(coe)_2RhCl]_2$,[19,20] and $[(coe)_2IrCl]_2$[19] were prepared by the literature procedures. All other reagents were purchased from Acros or Aldrich and used as received. Column chromatography was carried out using Macherey-Nagel silica gel 60 (0.04−0.063 mm particle size).

[(C_4Et_4)Rh(*p*-xylene)]PF_6 ([1a]PF_6). Complex $[(coe)_2RhCl]_2$ (216 mg, 0.30 mmol), $AgPF_6$ (168 mg, 0.66 mmol), and *p*-xylene (1 mL) were dissolved in nitromethane (1 mL), and the mixture was stirred for 3 h at room temperature. Then 3-hexyne (600 μL, 5.2 mmol, excess) was added, and the reaction mixture was stirred for 10 h at 60 °C (prolonged heating should be avoided because it leads to partial decomposition of PF_6^- anion). The precipitate of AgCl was removed by centrifugation and washed with CH_2Cl_2 (2 × 2 mL), and the combined solution was evaporated to dryness. The solid was reprecipitated from CH_2Cl_2/Et_2O and washed with Et_2O (2 × 5 mL) to give a brownish powder. This crude product was dissolved in CH_2Cl_2 and eluted through a silica gel column (8 × 1 cm) with a CH_2Cl_2/acetone mixture (10:1). Red-brown byproducts stayed on the column, while the pale yellow solution passed through. This solution was collected and evaporated to give pure [**1a**]PF_6 as an off-white, air-stable solid. Yield: 203 mg, 65%. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 6.91 (s, 4H, $C_6\underline{H}_4Me_2$), 2.42 (s, 6H, $C_6H_4\underline{Me}_2$), 2.20 (q, J = 7.5 Hz, 8H, CH_2^{C4Et4}), 1.12 (t, J = 7.5 Hz, 12H, CH_3^{C4Et4}). The spectral data were in accordance with those previously reported.[9a]

[(C_4Et_4)Rh(*tert*-butylbenzene)]PF_6 ([1b]PF_6). Complex $[(C_2H_4)_2RhCl]_2$ (59 mg, 0.15 mmol), $AgPF_6$ (85 mg, 0.33 mmol), and *tert*-butylbenzene (0.5 mL) were dissolved in acetone (1 mL), and the mixture was stirred for 2 h at room temperature. Then 3-hexyne (300 μL, 2.6 mmol, excess) was added, and the reaction mixture was stirred overnight. The precipitate of AgCl was removed by centrifugation, and the brown solution was evaporated to dryness. The solid was reprecipitated from CH_2Cl_2/Et_2O and washed with Et_2O (2 × 5 mL) to give [**1b**]PF_6 as a pale yellow, air-stable solid. Yield: 66 mg, 40%. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.17−7.25 (m, 2H, $C_6\underline{H}_5CMe_3$), 6.95−7.05 (m, 3H, $C_6\underline{H}_5CMe_3$), 2.25 (q, J = 7.5 Hz, 8H, CH_2^{C4Et4}), 1.42 (s, 9H, $C_6H_5C\underline{Me}_3$), 1.13 (t, J = 7.5 Hz, 12H, CH_3^{C4Et4}). ^{13}C NMR (101 MHz, $(CD_3)_2CO$): δ 101.1 (d, J = 4.4 Hz, $\underline{C}_6H_5CMe_3$), 99.8 (d, J = 4.1 Hz, $\underline{C}_6H_5CMe_3$), 99.5 (d, J = 3.9 Hz, $\underline{C}_6H_5CMe_3$), 98.5 (d, J = 11.9 Hz, $\underline{C}_4Et_4$), 34.5 (s, $C_6H_5\underline{C}Me_3$), 30.2 (s, $C_6H_5C\underline{Me}_3$), 19.0 (s, CH_2^{C4Et4}), 13.1 (s, CH_3^{C4Et4}). Anal. Calcd for $C_{22}H_{34}F_6RhP$: C, 48.36; H, 6.27. Found: C, 48.35; H, 6.25.

[(C_4Et_4)Rh(mesitylene)]PF_6 ([1c]PF_6). Complex $[(C_2H_4)_2RhCl]_2$ (39 mg, 0.10 mmol), $AgPF_6$ (56 mg, 0.22 mmol), and mesitylene (0.5 mL) were dissolved in nitromethane (1 mL), and the mixture was stirred for 2 h at room temperature. Then 3-hexyne (200 μL, 1.7 mmol, excess) was added, and the reaction mixture was stirred overnight. The precipitate of AgCl was removed by centrifugation, and the brown solution was evaporated to dryness. The solid was reprecipitated from CH_2Cl_2/Et_2O and washed with Et_2O (2 × 5 mL) to give [**1c**]PF_6 as an off-white air-stable solid. Yield: 45 mg, 42%. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 6.81 (s, 3H, $C_6\underline{H}_3Me_3$), 2.42 (s, 9H, $C_6H_3\underline{Me}_3$), 2.16 (q, J = 7.5 Hz, 8H, CH_2^{C4Et4}), 1.12 (t, J = 7.5 Hz, 12H, CH_3^{C4Et4}). The spectral data were in accordance with those previously reported.[9a]

[(C_4Et_4)Rh(4-mesitylbutanoic acid)]PF_6 ([1d]PF_6). Complex $[(C_2H_4)_2RhCl]_2$ (39 mg, 0.10 mmol), $AgPF_6$ (56 mg, 0.22 mmol), and 4-mesitylbutanoic acid (206 mg, 1 mmol) were dissolved in nitromethane (1 mL), and the mixture was stirred for 2 h at room temperature. Then 3-hexyne (200 μL, 1.7 mmol, excess) was added, and reaction mixture was stirred overnight. The precipitate of AgCl was removed by centrifugation, and the brown solution was evaporated to dryness. The solid was reprecipitated from CH_2Cl_2/hexanes and filtered through a short pad of silica gel (eluent CH_2Cl_2/acetone, 5:1). Solvent was evaporated to give [**1d**]PF_6 as a pale brown, air-stable, oily substance. Yield: 59 mg, 48%. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 6.82 (s, 2H, $C_6\underline{H}_2Me_3(CH_2)_3COOH$), 2.80 (m, 2H, $C_6H_2Me_3(\underline{CH}_2)_3COOH$), 2.50 (m, 8H, $C_6H_2\underline{Me}_3(\underline{CH}_2)_3COOH$ overlapped), 2.38 (s, 3H, $C_6H_2\underline{Me}_3(CH_2)_3COOH$), 2.13 (q, J = 7.5 Hz, 8H, CH_2^{C4Et4}), 1.85 (m, 2H, $C_6H_2Me_3(\underline{CH}_2)_3COOH$), 1.12 (t, J = 7.5 Hz, 12H, CH_3^{C4Et4}). ^{13}C NMR (101 MHz, $(CD_3)_2CO$): δ 173.3 (s, $C_6H_2Me_3(CH_2)_3\underline{C}OOH$), 116.4 (m, $\underline{C}_6H_2Me_3(CH_2)_3COOH$), 114.4 (m, $\underline{C}_6H_2Me_3(CH_2)_3COOH$), 113.8 (m, $\underline{C}_6H_2Me_3(CH_2)_3COOH$), 108.8 (m, $\underline{C}_6H_2Me_3(CH_2)_3COOH$), 95.4 (d, J = 11.9 Hz, $\underline{C}_4Et_4$), 32.6 (s, $C_6H_2Me_3(\underline{CH}_2)_3COOH$), 27.4 (s, $C_6H_2Me_3(\underline{CH}_2)_3COOH$), 23.4 (s, $C_6H_2Me_3(\underline{CH}_2)_3COOH$), 18.1 (s, $C_6H_2\underline{Me}_3(CH_2)_3COOH$), 18.0 (s, CH_2^{C4Et4}), 17.3 (s, $C_6H_2\underline{Me}_3(CH_2)_3COOH$), 12.8 (s, CH_3^{C4Et4}).

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Anal. Calcd for $C_{25}H_{38}F_6O_2PRh$: C, 48.55; H, 6.19. Found: C, 47.83; H, 5.91. Correct elemental analysis was difficult to obtain because the compound was oily. Complex [**1d**]BF_4 was prepared similarly, using $AgBF_4$ instead of $AgPF_6$. Crystals of [**1d**]BF_4 were obtained by slow diffusion of Et_2O vapors into the solution of the complex in CH_2Cl_2.

[(C_4Et_4)Rh(C_6Et_6)]PF_6 ([1e]PF_6). Complex $[(coe)_2RhCl]_2$ (72 mg, 0,10 mmol) and $AgPF_6$ (56 mg, 0.22 mmol) were dissolved in acetone (2 mL), and the mixture was stirred for 2 h at room temperature. Then 3-hexyne (500 μL, 4.3 mmol, excess) was added, and reaction mixture was stirred overnight at 60 °C. The precipitate of AgCl was removed by centrifugation, and the brown solution was evaporated to dryness. The solid was reprecipitated from CH_2Cl_2/Et_2O and washed with Et_2O (3 × 5 mL) to give [**1e**]PF_6 as a pale yellow, air-stable solid. Yield: 92 mg, 70%. [**1e**]OTf was prepared similarly, using AgOTf instead of $AgPF_6$. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 2.83 (q, J = 7.5 Hz, 12H, CH_2^{C6Et6}), 2.05 (q, J = 7.5 Hz, 8H, CH_2^{C4Et4}), 1.38 (t, J = 7.5 Hz, 18H, CH_3^{C6Et6}), 1.10 (t, J = 7.5 Hz, 12H, CH_3^{C4Et4}). ^{13}C NMR (101 MHz, $(CD_3)_2CO$): δ 118.6 (d, J = 4.0 Hz, $\underline{C}_6Me_6$), 94.0 (d, J = 11.6 Hz, $\underline{C}_4Et_4$), 22.0 (s, CH_2^{C6Et6}), 18.2 (s, CH_2^{C4Et4}), 15.7 (s, CH_3^{C6Me6}), 13.0 (s, CH_3^{C4Et4}). Anal. Calcd for $C_{31}H_{50}F_3O_3RhS$: C, 56.18; H, 7.60. Found: C, 56.48; H, 7.52.

[(C_4Et_4)Rh(*p*-methylaniline)]PF_6 ([1f]PF_6). Complex [**1a**]PF_6 (52 mg, 0.1 mmol) and *p*-methylaniline (107 mg, 1 mmol) were dissolved in acetone (2 mL) and refluxed for 18 h. Solvent was evaporated to dryness, and the solid was washed with Et_2O (2 × 5 mL) and reprecipitated from CH_2Cl_2/Et_2O to give [**1f**]PF_6 as a pale yellow, air-stable solid. Yield: 46 mg, 88%. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 6.64 (d, J = 6.8 Hz, 2H, 4-Me$C_6\underline{H}_4NH_2$), 6.44 (d, J = 7.0 Hz, 2H, 4-Me$C_6\underline{H}_4NH_2$), 5.73 (s, 2H, 4-Me$C_6H_4N\underline{H}_2$), 2.28 (s, 3H, 4-$\underline{Me}C_6H_4NH_2$), 2.14 (q, J = 7.5 Hz, 8H, CH_2^{C4Et4}), 1.11 (t, J = 7.5 Hz, 12H, CH_3^{C4Et4}). ^{13}C NMR (101 MHz, $(CD_3)_2CO$): δ 134.2 (s, 4-Me$\underline{C}_6H_4NH_2$), 106.2 (d, J = 4.5 Hz, 4-Me$\underline{C}_6H_4NH_2$), 100.8 (d, J = 4.8 Hz, 4-Me$\underline{C}_6H_4NH_2$), 95.1 (d, J = 11.9 Hz, $\underline{C}_4Et_4$), 85.6 (m, 4-Me$\underline{C}_6H_4NH_2$), 18.4 (s, CH_2^{C4Et4}), 17.7(s, 4-$\underline{Me}C_6H_4NH_2$), 12.8 (s, CH_3^{C4Et4}). Anal. Calcd for $C_{19}H_{29}F_6NPRh$: C, 43.94; H, 5.63; N, 2.70. Found: C, 43.84; H, 5.62; N, 2.61.

[(C_4Et_4)Rh(2-mesitylacetonitrile)]PF_6 ([1g]PF_6). Complex [**1a**]PF_6 (52 mg, 0.1 mmol) and 2-mesitylacetonitrile (158 mg, 1 mmol) were dissolved in acetone (2 mL) and refluxed for 18 h. Solvent was evaporated, and the brown oil was washed with Et_2O (3 × 5 mL), dissolved in CH_2Cl_2, and eluted through a short pad of silica gel with a CH_2Cl_2/acetone (5:1) mixture. Eluent was evaporated, and the residue was reprecipitated several times from CH_2Cl_2/Et_2O to give [**1g**]PF_6 as a colorless, air-stable, oily substance. Yield: 34 mg, 60%. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 6.97 (s, 2H, $Me_3C_6\underline{H}_2CH_2CN$), 4.16 (d, J = 2.5 Hz, 2H, $Me_3C_6H_2C\underline{H}_2CN$), 2.59 (s, 6H, $\underline{Me}_3C_6H_2CH_2CN$), 2.42 (s, 3H, $\underline{Me}_3C_6H_2CH_2CN$), 2.19 (q, J = 7.5 Hz, 8H, CH_2^{C4Et4}), 1.12 (t, J = 7.5 Hz, 12H, CH_3^{C4Et4}). ^{13}C NMR (101 MHz, $(CD_3)_2CO$): δ 116.9 (s, $Me_3C_6H_2CH_2\underline{C}N$), 116.3 (d, J = 4.1 Hz, $Me_3\underline{C}_6H_2CH_2CN$), 116.0 (d, J = 3.9 Hz, $Me_3\underline{C}_6H_2CH_2CN$), 107.8 (d, J = 4.4 Hz, $Me_3\underline{C}_6H_2CH_2CN$), 104.9 (d, J = 4.2 Hz, $Me_3\underline{C}_6H_2CH_2CN$), 97.9 (d, J = 11.7 Hz, $\underline{C}_4Et_4$), 19.1 (s, $\underline{Me}_3C_6H_2CH_2CN$), 18.9 (s, CH_2^{C4Et4}), 18.6 (s, $\underline{Me}_3C_6H_2$-CH_2CN), 17.3 (s, $Me_3C_6H_2\underline{C}H_2CN$), 13.7 (s, CH_3^{C4Et4}). Anal. Calcd for $C_{23}H_{33}F_6NPRh$: C, 48.35; H, 5.82. Found: C, 48.36; H, 6.25.

[(C_2H_4)$_2$Rh(C_6Me_6)]PF_6 ([2]PF_6). Complex $[(C_2H_4)_2RhCl]_2$ (98 mg, 0.25 mmol), $AgPF_6$ (146 mg, 0.57 mmol), and hexamethylbenzene (416 mg, 2.6 mmol, excess) were dissolved in acetone/CH_2Cl_2 (1:1, 2 mL, CH_2Cl_2 improves solubility of C_6Me_6), and the mixture was stirred overnight. The precipitate of AgCl was removed by centrifugation and washed with CH_2Cl_2, and the combined yellow solution was evaporated to dryness. The solid was reprecipitated from CH_2Cl_2/Et_2O and washed with Et_2O (3 × 5 mL) to give the product. Yield: 166 mg, 84%. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 2.78 (br d, J = 12.5 Hz, 4H, CH_2), 2.41 (br d, J = 12.5 Hz, 4H, CH_2), 2.36 (s, 18H, CH_3). The spectral data are similar to those previously reported.[13,21] Crystals of [**2**]PF_2O_2 were obtained by slow diffusion of Et_2O vapors into the solution of [**2**]PF_6 in acetone.

[(coe)$_2$Rh(*p*-xylene)]PF_6 ([3]PF_6). Complex $[(coe)_2RhCl]_2$ (36 mg, 0.05 mmol), $AgPF_6$ (28 mg, 0.11 mmol), and *p*-xylene (0.5 mL) were dissolved in nitromethane (0.5 mL), and the mixture was left stirring overnight. The precipitate of AgCl was removed by centrifugation, and the yellow solution was evaporated to dryness. The solid was reprecipitated from CH_2Cl_2/Et_2O and washed with Et_2O (2 × 5 mL) to give [**3**]PF_6 as a pale yellow solid. This compound is stable in air for several days, but notably decomposes (forms insoluble species) after several months. Yield: 45 mg, 78%. ^{1}H NMR (400 MHz, CD_3NO_2): δ 6.51 (s, 4H, $C_6\underline{H}_4Me_2$), 3.13 (d, J = 9.3 Hz, 4H, CH^{C8H14}), 2.77 (s, 6H, $C_6H_4\underline{Me}_2$), 2.62 (dd, J = 12.3, 2.9 Hz, 4H, CH_2^{C8H14}), 2.00−1.93 (m, 8H, CH_2^{C8H14}), 1.72−1.58 (m, 12H, CH_2^{C8H14}). ^{13}C NMR (101 MHz, CD_3NO_2): δ 124.0 (s, $C^{C6H4Me2}$), 107.5 (s, $CH^{C6H4Me2}$), 78.8 (d, J = 12.5 Hz, CH^{C8H14}), 31.4 (s, CH_2^{C8H14}), 31.1 (s, CH_2^{C8H14}), 25.8 (s, CH_2^{C8H14}), 17.9 (s, $CH_3^{C6H4Me2}$). Anal. Calcd for $C_{24}H_{38}F_6RhP\cdot Et_2O$: C, 51.85; H, 7.46. Found: C, 51.39; H, 6.96.

[(coe)$_2$Ir(*p*-xylene)]PF_6 ([4]PF_6). Complex $[(coe)_2IrCl]_2$ (45 mg, 0.05 mmol), $AgPF_6$ (30 mg, 0.12 mmol), and an excess of *p*-xylene (0.5 mL) were dissolved in dichloromethane (2 mL) and stirred overnight at room temperature. The precipitate of AgCl was removed by centrifugation, and the yellow solution was evaporated to dryness. The residue was reprecipitated from CH_2Cl_2/petroleum ether and washed with petroleum ether (3 × 5 mL) to give [**4**]PF_6 as a beige solid. This compound is stable in air for several days, but notably decomposes (forms insoluble species) after several months. Yield: 42 mg, 64%. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 6.63 (s, 4H, $C_6\underline{H}_4Me_2$), 2.55 (s, 6H, $C_6H_4\underline{Me}_2$), 2.44 (d, J = 9.9 Hz, 4H, CH^{C8H14}), 2.33 (dd, J = 12.9, 2.5 Hz, 4H, CH_2^{C8H14}), 1.81−1.67 (m, 8H, CH_2^{C8H14}), 1.50−1.35 (m, 12H, CH_2^{C8H14}). ^{13}C NMR (101 MHz, $(CD_3)_2CO$): δ 120.3 (s, $\underline{C}_6H_4Me_2$), 101.4 (s, $\underline{C}_6H_4Me_2$), 62.9 (s, CH^{C8H14}), 32.7 (s, CH_2^{C8H14}), 31.7 (s, CH_2^{C8H14}), 26.5 (s, CH_2^{C8H14}), 18.6 (s, $C_6H_4\underline{Me}_2$). Anal. Calcd for $C_{24}H_{38}F_6IrP\cdot CH_2Cl_2$: C, 40.11; H, 5.39. Found: C, 40.22; H, 5.61.

[(C_4Et_4)Ir(C_6Et_6)]PF_6 ([5]PF_6). Complex $[(coe)_2IrCl]_2$ (45 mg, 0.05 mmol) and $AgPF_6$ (30 mg, 0.12 mmol) were dissolved in 1,2-dichloroethane (2 mL) and vigorously stirred for 5 min at room temperature. Then 3-hexyne (400 μL, 3.5 mmol, excess) was added, and reaction mixture was stirred at 80 °C for 6 h. The precipitate of AgCl was removed by centrifugation, and the brown solution was evaporated to dryness. The solid was reprecipitated from CH_2Cl_2/Et_2O and washed with Et_2O (3 × 5 mL) to give [**5**]PF_6 as a beige, oily yellow, air-stable solid. The product was then dissolved in a minimal amount of CH_2Cl_2 and crystallized by slow diffusion of Et_2O vapors. Yield: 49 mg, 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.63 (q, J = 7.4 Hz, 12H, CH_2^{C6Et6}), 1.92 (q, J = 7.4 Hz, 8H, CH_2^{C4Et4}), 1.37 (t, J = 7.4 Hz, 18H, CH_3^{C6Et6}), 1.08 (t, J = 7.4 Hz, 12H, CH_3^{C4Et4}). ^{13}C NMR (101 MHz, $(CD_3)_2CO$): δ 110.8 (s, $\underline{C}_6Et_6$), 84.7 (s, $\underline{C}_4Et_4$), 22.9 (s, CH_2^{C6Et6}), 18.3 (s, CH_2^{C4Et4}), 16.4 (s, CH_3^{C6Et6}), 14.7 (s, CH_3^{C4Et4}). Anal. Calcd for $C_{30}H_{50}F_6IrP$: C, 48.18; H, 6.74. Found: C, 48.50; H, 6.39.

[(C_4Ph_4)Ir(*p*-xylene)]$^+$ ([6]PF_6). Complex $[(coe)_2IrCl]_2$ (45 mg, 0.05 mmol), $AgPF_6$ (30 mg, 0.12 mmol), and *p*-xylene (0.5 mL) were dissolved in 1,2-dichloroethane (2 mL), and the mixture was stirred for 2 h at room temperature. Then diphenylacetylene (107 mg, 0.6 mmol) was added, and reaction mixture was heated at 80 °C for 12 h. The precipitate of AgCl was removed by centrifugation, and the brown solution was evaporated to dryness. The solid was reprecipitated from CH_2Cl_2/Et_2O and washed with Et_2O (3 × 5 mL) to give the product [**6**]PF_6 as a beige solid. Yield: 18 mg, 23%. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.39 (m, 20H, CH^{Ph}), 7.11 (s, 4H, $CH^{C6H4Me2}$), 1.96 (s, 6H, $CH_3^{C6H4Me2}$). ^{13}C NMR (101 MHz, CD_3NO_2): δ 129.3 (s, Ph^{C4Ph4}), 129.1 (s, Ph^{C4Ph4}), 129.1 (s, Ph^{C4Ph4}), 110.5 (s, $\underline{C}_6H_4Me_2$), 94.2 (s, $\underline{C}_4Ph_4$), 82.4 (s, $\underline{C}_6H_4Me_2$), 16.4 (s, $CH_3^{C6H4Me2}$). Correct analysis could not be obtained, apparently, because of the slow decomposition of the substance.

General Procedure for Catalytic Reductive Amination. A 2 mL glass vial was placed in a 10 mL stainless steel autoclave and charged with the catalyst (0.005 mmol, 1.0 mol %), *p*-anisidine (62 mg, 0.5 mmol), *p*-tolylaldehyde (59 μL, 0.5 mmol), and *tert*-butanol (0.5 mL). The use of a glass vial is crucial because interaction of the catalyst with the metal surface of the autoclave led to decreased

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catalytic activity. The autoclave was sealed, flushed twice with 10 bar of CO, and then charged with 3 bar of CO. The autoclave was placed into a preheated (100 °C) oil bath and after 24 h was cooled to room temperature and depressurized. The mixture was then analyzed by ^{1}H NMR. Full conversion of the starting materials was observed. Depending on the catalyst the yield of **13** was 89% (**1a**), 95% (**1f**), 96% (for **2**), and 92% (for **3**). For the product **13** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 7.7 Hz, 2H, CH), 7.19 (d, J = 7.7 Hz, 2H, CH), 6.82 (d, J = 8.8 Hz, 2H, CH), 6.63 (d, J = 8.8 Hz, 2H, CH), 4.26 (s, 2H, CH_2), 3.77 (s, 3H, OCH_3), 2.39 (s, 3H, $ArCH_3$). The spectral data were in accordance with those previously reported.[9b]

Computational Details. Geometry optimizations were performed without symmetry constraints using the PBE exchange−correlation functional[22] and all-electron triple-ζ basis set 3z (similar to TZ2P) implemented in the Priroda 6 code (H {5s1p}/[3s1p], C {11s6p2d}/[6s3p2d], Rh {20s16p11d}/[14s11p7d]).[23] Frequency calculations were performed to confirm the nature of the stationary points. The paths of the reactions were traced from the transition states to the products and to the reactants using the intrinsic reaction coordinate method.[24] The ChemCraft software (http://www.chemcraftprog.com) was used for molecular modeling.

In order to estimate the accuracy of the chosen PBE/3z level, we calculated the gas-phase enthalpy of ethylene dissociation in the complex $CpRh(C_2H_4)_2$. The calculated value of 33.1 kcal mol^{-1} was found to be close to the experimental one of 31 kcal mol^{-1}.[25] Nevertheless, the free energy values given in this paper should be considered only as estimates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00539.

NMR spectra (PDF)

Crystallographic data (CIF)

Cartesian coordinates for optimized structures, which may be opened as a text file to read the coordinates or opened directly by a molecular modeling program such as Mercury (version 3.3 or later, http://www.ccdc.cam.ac.uk/pages/Home.aspx) for visualization and analysis (XYZ)

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Notes

The authors declare no competing financial interest.

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