Synthesis, Characterization, and Thermal Stability of $(\eta^6{:}\eta^1\text{-}C_6H_5CH_2CH_2PR_2)Ru(CH_3)_2$ (R = Cy, Ph, Et)

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Several new arene−phosphine ligands were synthesized and used to prepare the following series of tethered dialkylruthenium(II) complexes: $(\eta^6{:}\eta^1\text{-}C_6H_5CH_2CH_2PR_2)Ru(CH_3)_2$, where R = Cy (**1**), Ph (**2**), Et (**3**). The structures of complexes **1** and **2** were determined by X-ray diffraction. While complexes **1** and **2** were found to be more thermally stable than analogous nontethered analogues, complex **3** was found to decompose at room temperature. In preliminary studies, the use of complexes **1** and **2** as catalyst precursors for the polymerization of ethylene was examined.

Introduction

Early-transition-metal alkyl complexes have been widely studied, at least in part, because they serve as important catalyst precursors for the polymerization of olefins.[1,2] Recent research, however, has focused on the development of new types of Ziegler−Natta catalysts based on late transition metals because of the anticipated tolerance of these metals toward polar functional groups.[3−18] In particular, several new catalysts that oligomerize and/or polymerize olefins have been recently developed based on group VIII−X metals such as Fe,[3−9] Co,[3−5,8] Rh,[10] Ni,[11−18] and Pd.[12−14] Despite these advances, there are relatively few examples of ruthenium-based Ziegler−Natta catalysts.[19−22]

Because ruthenium complexes have been shown to exhibit a high tolerance toward polar functional groups in the ring-opening metathesis polymerization (ROMP) of cyclic olefins,[23−28] we have been exploring the development of ruthenium-based Ziegler−Natta polymerization catalysts.[29,30] In particular, our research has found that the abstraction of one of the cis methyl groups of *cis*-$(DMPE)_2RuMe_2$ in the presence of ethylene affords the cation *trans*-$[(DMPE)_2RuMe(CH_2{=}CH_2)]^+$, which fails to insert ethylene into the remaining Ru−methyl bond.[30] One of the major drawbacks of this system apparently derives from the rapid isomerization of the bidentate phosphine ligand during cation formation, which gives rise to an inaccessible trans location of the Ru−methyl bond relative to the coordinated ethylene group.

From these observations, we concluded that it should be possible to lock the vacant orbital cis to an alkyl group by employing a rigid ligand system incapable of isomerization. To this end, we have designed a family

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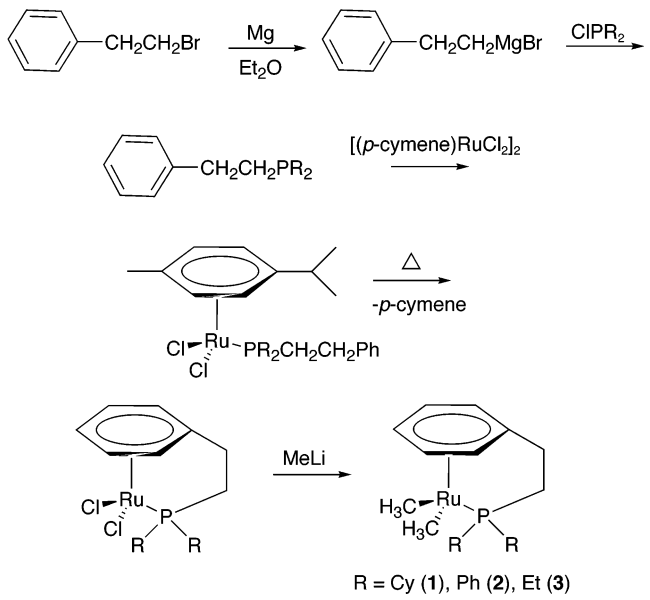
Scheme 1



of dimethylruthenium(II) complexes containing the unique arene−phosphine ligand, $C_6H_5CH_2CH_2PR_2$, where R = Cy, Ph, Et. We specifically targeted the study of (η^6: η^1-$C_6H_5CH_2CH_2PR_2$)$Ru(CH_3)_2$ complexes because the abstraction of a single methyl group from these substrates would necessarily afford a vacant site cis to the residual methyl group. Moreover, the resultant cationic intermediates would be isolobal with those postulated in the catalytically active [$CpCoH(C_2H_4)$-PR_3]$^+$ olefin polymerization systems.[31] Furthermore, we believed that it might be possible to achieve stereospecific catalysis arising from the C_1 symmetry of the metal center in specially designed analogues.[32]

In this paper, we describe the synthesis and characterization of a new family of complexes, (η^6: η^1-$C_6H_5CH_2$-CH_2PR_2)$Ru(CH_3)_2$, where R = Cy (**1**), Ph (**2**), Et (**3**). Through a series of thermal decomposition studies, we then compare the thermal stabilities of these complexes to each other and to those of known nontethered analogues such as (η^6-C_6H_6)$RuMe_2(PPh_3)$ and (η^6-1,3,5-$C_6H_3Me_3$)$RuMe_2(PMe_2Ph)$.[33] Furthermore, we conduct preliminary experiments in which complexes **1** and **2** are examined for use as Ziegler−Natta catalyst precursors for the polymerization of ethylene.

Results and Discussion

Synthesis of Complexes 1−3. Scheme 1 illustrates the strategy used to synthesize complexes **1**−**3**. In the first step, a series of new arene−phosphine ligands were prepared by the reaction of (2-phenylethyl)magnesium bromide with the appropriate dialkylchlorophosphines in diethyl ether. These ligands were subsequently treated with [(*p*-cymene)$RuCl_2]_2$ in refluxing benzene to give the orange-red nontethered complexes (*p*-cymene)-$RuCl_2(PR_2CH_2CH_2C_6H_5)$ (R = Cy, Ph, Et) in greater than 90% yield. Subsequent heating of the nontethered complexes in refluxing chlorobenzene led to the replacement of the cymene ligand with the phenyl moiety of the phosphine ligand to give the tethered dichloro complexes (η^6:η^1-$C_6H_5CH_2CH_2PR_2$)$RuCl_2$ (R = Cy, Ph, Et) in 60−95% yield. Alkylation of these complexes with excess methyllithium in diethyl ether gave the targeted dialkyl complexes (η^6: η^1-$C_6H_5CH_2CH_2PR_2$)$Ru(CH_3)_2$ (R = Cy, Ph, Et) in ∼35% yield. We found that the use of less than 5 equiv of methyllithium led to incomplete alkylation (e.g., monomethylated Ru side products). We isolated pure samples of (η^6: η^1-$C_6H_5CH_2CH_2PCy_2$)-$Ru(CH_3)_2$ (**1**) and (η^6: η^1-$C_6H_5CH_2CH_2PPh_2$)$Ru(CH_3)_2$ (**2**) by use of flash chromatography through particulate Al_2O_3. We were, however, unable to isolate pure samples of (η^6: η^1-$C_6H_5CH_2CH_2PEt_2$)$Ru(CH_3)_2$ (**3**) due to its rapid decomposition during flash chromatography. Complexes **1**−**3** were soluble in CH_2Cl_2, benzene, and toluene and slightly soluble in diethyl ether.

Characterization of Complexes 1−3. Analysis by ^{1}H NMR spectroscopy of **1**−**3** in CD_2Cl_2 showed that the coordinated arene exhibits three well-separated resonances in the region δ 4.5−5.5 (for **1**, δ 5.13 (t), 4.97 (d), 4.53 (t); for **2**, δ 5.42 (t), 5.10 (d), 4.88 (t); for **3**, δ 5.04 (t), 4.65 (t), 4.53 (d)). The doublets at δ −0.02 for **1**, δ −0.20 for **2**, and δ 0.50 for **3** correspond to the Ru−CH_3 protons coupled to the phosphine nucleus. The coupling constants (J_{HP}) of these doublets were 4.8, 6.0, and 5.7 Hz for **1**−**3**, respectively, which is consistent with values reported for related compounds such as (η^6-C_6H_6)$RuMe_2(PPh_3)$,[33] (η^6-1,3,5-$C_6H_3Me_3$)$RuMe_2(PMe_2Ph)$,[33] (η^6-C_6Me_6)$RuMe_2$(L) (where L = PMe_3, $PMePh_2$, PPh_3),[34] and [(η^6-C_6Me_6)$RuMe(PMe_3)(CO)]^+$.[35]

We performed X-ray structural analyses of crystals of **1** and **2** generated by the slow evaporation of CH_2Cl_2 from concentrated solutions containing the respective complexes. We were, however, unable to obtain crystals of **3**, despite using a variety of solvent and mixed-solvent systems during crystallization trials. Thermal ellipsoid plots and views perpendicular to the η^6-phenyl ring for compounds **1** and **2** are shown in Figures 1 and 2, respectively. Selected bond distances and angles are provided in Tables 1 and 2, respectively. The phenyl ring and ethylene bridge of compound **1** were disordered 60:40 over two positions approximately related by a mirror plane. In contrast, the structure of compound **2** was well ordered.

The Ru−C(1) and Ru−C(2) bond distances were similar in both compounds (2.136(4) and 2.129(4) Å for **1**; 2.142(4) and 2.143(4) Å for **2**). These values are comparable to those reported in the literature for ruthenium alkyls.[33,34] The bond distances from Ru to each carbon of the coordinated arene were as follows for **1**: 2.210(8) Å, Ru−C(5); 2.240(9) Å, Ru−C(6); 2.27(1) Å, Ru−C(7); 2.268(8) Å, Ru−C(8); 2.238(6) Å, Ru−C(9); 2.209(7) Å, Ru−C(10). The analogous distances were as follows for **2**: 2.181(3) Å, Ru−C(13); 2.250(4) Å, Ru−C(14); 2.215(4) Å, Ru−C(15); 2.237(4) Å, Ru−C(16); 2.239(3) Å, Ru−C(17); 2.262(4) Å, Ru−C(18). In both complexes, the ruthenium metal lies beneath the center of the coordinated arene. The elongated Ru−carbon bonds trans to the bridge and the

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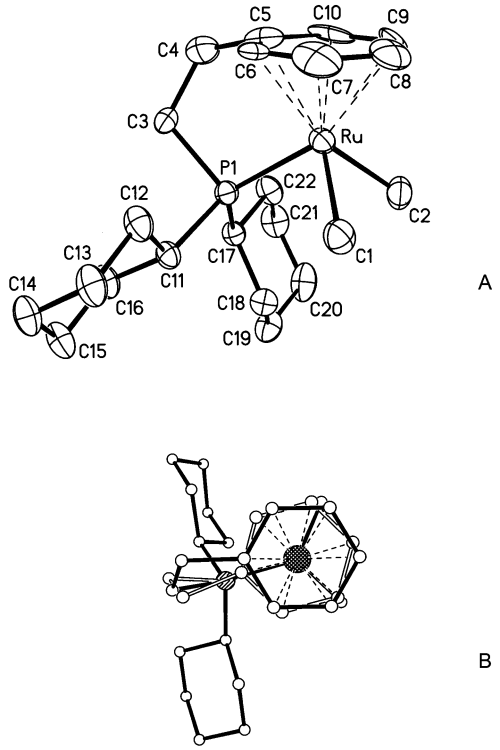

Figure 1. (A) Thermal ellipsoid plot of the complex (η^6:η^1-$C_6H_5CH_2CH_2PCy_2$)$Ru(CH_3)_2$ (**1**) at the 40% probability level and (B) a view perpendicular to the η^6-phenyl ring.

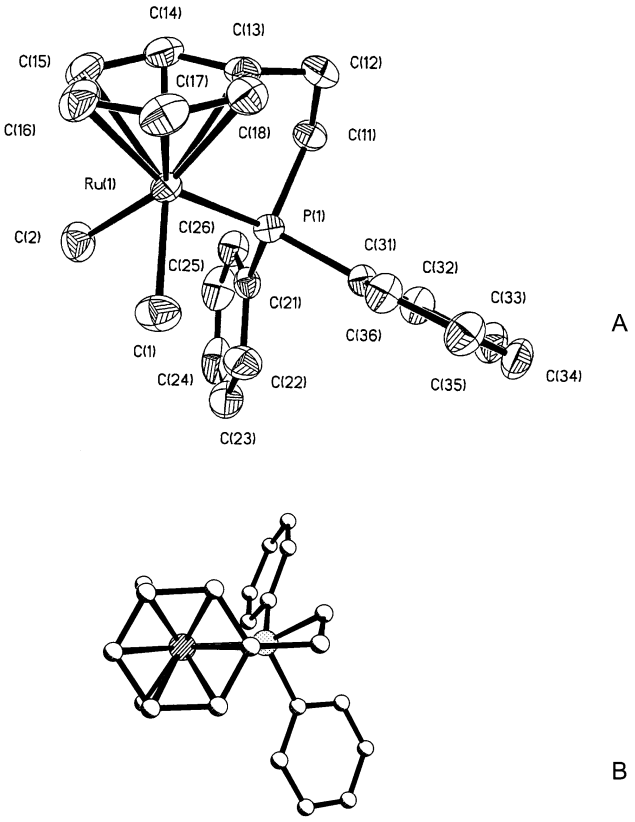

Figure 2. (A) Thermal ellipsoid plot of the complex (η^6:η^1-$C_6H_5CH_2CH_2PPh_2$)$Ru(CH_3)_2$ (**2**) at the 40% probability level and (B) a view perpendicular to the η^6-phenyl ring.

shortened Ru−carbon bonds adjacent to the bridge probably arise from distortion of the coordinated arene induced by the presence of the two-carbon bridge. Similar distortion was observed in the related dichloro complexes (η^6:η^1-$C_6H_5(CH_2)_3PPh_2$)$RuCl_2$[36] and (*o*-$HOCH_2$-η^6:η^1-$C_6H_4CH_2CH_2PPh_2$)$RuCl_2$.[37] While the three ligands (CH_3, CH_3, P) of compound **2** lie in an eclipsed conformation relative to the coordinated arene, those of compound **1** are either eclipsed or slightly staggered relative to the coordinated arene, depending on the nature of the disordered structure.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1

Bond Lengths			
Ru−C(1)	2.136(4)	Ru−C(2)	2.129(4)
Ru−C(5)	2.210(8)	Ru−C(6)	2.240(9)
Ru−C(7)	2.268(10)	Ru−C(8)	2.268(8)
Ru−C(9)	2.238(6)	Ru−C(10)	2.209(7)
Ru−P(1)	2.3070(11)		
Bond Angles			
C(1)−Ru−C(2)	81.20(18)	C(1)−Ru−C(5)	146.4(3)
C(2)−Ru−C(5)	132.4(3)	C(1)−Ru−C(6)	110.9(3)
C(2)−Ru−C(6)	163.5(2)	C(1)−Ru−C(7)	90.3(3)
C(2)−Ru−C(7)	137.7(3)	C(1)−Ru−C(8)	96.7(3)
C(2)−Ru−C(8)	103.9(3)	C(1)−Ru−C(9)	125.7(3)
C(2)−Ru−C(9)	87.1(2)	C(1)−Ru−C(10)	161.5(3)
C(2)−Ru−C(10)	99.3(3)	C(1)−Ru−P(1)	90.78(11)
C(2)−Ru−P(1)	97.68(12)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2

Bond Lengths			
Ru−C(1)	2.142(4)	Ru−C(2)	2.143(4)
Ru−C(13)	2.181(3)	Ru−C(14)	2.250(4)
Ru−C(15)	2.215(4)	Ru−C(16)	2.237(4)
Ru−C(17)	2.239(3)	Ru−C(18)	2.262(4)
Ru−P(1)	2.263(1)		
Bond Angles			
C(1)−Ru−C(2)	81.65(16)	C(2)−Ru−C(13)	136.25(14)
C(1)−Ru−C(13)	141.20(15)	C(2)−Ru−C(15)	88.80(15)
C(1)−Ru−C(15)	134.13(16)	C(2)−Ru−C(16)	102.97(17)
C(1)−Ru−C(16)	102.22(15)	C(2)−Ru−C(17)	136.70(16)
C(1)−Ru−C(17)	91.15(15)	C(2)−Ru−C(14)	103.09(15)
C(1)−Ru−C(14)	168.32(14)	C(2)−Ru−C(18)	166.69(16)
C(1)−Ru−C(18)	107.44(15)	C(1)−Ru−P(1)	92.14(11)
C(2)−Ru−P(1)	90.42(12)		

Thermal Stability of Complexes 1 and 2. We examined the thermal stability of complexes **1** and **2** both in solution and in the solid state. Due to our inability to purify complex **3** (vide supra) and the unknown manner by which the impurities might influence its apparent thermal stability, we chose to exclude complex **3** from these studies. Crystals of complex **1** were found to be stable over several months at room temperature under an inert atmosphere. Crystals of complex **2**, however, gradually decomposed over a period of 1 month under the same conditions. The stability of the compounds in solution was monitored by ^{1}H NMR spectroscopy. Compounds **1** and **2** were dissolved in dry, oxygen-free *o*-xylene-d_{10} in an NMR tube. The NMR tube was then sealed under vacuum and gradually heated to 130 °C. The concentrations of **1** and **2** were measured by integration of the peaks due to the η^6-C_6H_5 moiety at δ 5.12 for **1** and at δ 5.32 for **2** using C_6Me_6 (0.001 M) as an internal standard. When the solution was heated for several hours, its color gradually changed from light yellow to orange and eventually to black.

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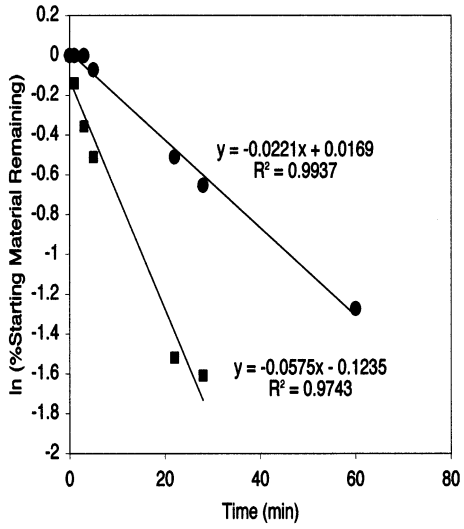

Figure 3. Thermal decomposition profiles of (η^6:η^1-$C_6H_5CH_2CH_2PR_2$)$Ru(CH_3)_2$, where R = Cy (●), Ph (■).

The intensities of all ^{1}H NMR resonances attributed to **1** and **2** were observed to gradually decrease with heating over time. New resonances at δ 0.43 (s) and 7.5 (broad m) appeared after 22 h for **1** and 5 h for **2**. Line broadening over the range δ 0−3.5 was observed for both species, perhaps suggesting the formation of paramagnetic decomposition products. Figure 3 shows that the decomposition of **1** and **2** exhibited first-order kinetics, as measured quantitatively by ^{1}H NMR spectroscopy. The rate constants at 130 °C were calculated to be 2.21×10^{-2} min^{-1} with $t_{1/2} = 31$ min for compound **1** and 5.75×10^{-2} min^{-1} with $t_{1/2} = 12$ min for compound **2**. While we were unable to characterize fully the decomposition products, we believe that the decomposition reactions proceed via the formation of methane and displacement of the coordinated arene, because of the appearance of the singlet at δ 0.43 (corresponding to free methane)[38] and the broad multiplet at δ 7.5 (uncoordinated aromatic) as described above. It is possible that the methane is generated via α-hydride transfer from one methyl group to another and a radical reaction—a process similar to that observed in studies of the thermal decomposition of diethylruthenium(IV) porphyrin complexes.[39] Although we attempted to further characterize the decomposition reactions by UV spectroscopy, the stronger absorption band of the decomposed products (λ_{max} 267) overlapped that of the starting materials (λ_{max} ~270) and thus prevented a detailed analysis.

Although the complexes (η^6-C_6Me_6)$RuMe_2$(L), where L = PMe_3, $PMePh_2$, PPh_3, were reportedly isolable at room temperature,[34] separate studies showed that the related nontethered complexes (η^6-C_6H_6)$RuMe_2(PPh_3)$ and (η^6-1,3,5-$C_6H_3Me_3$)$RuMe_2(PMe_2Ph)$ could not be isolated at room temperature due to their facile decomposition.[33] Given that the structures of the last two complexes more closely resemble the structures of **1**−**3**, the results presented here provide strong evidence that the new tethered arene−phosphine dialkylruthenium complexes are more thermally stable than analogous nontethered systems.

Attempted Polymerization of Ethylene Using Complexes 1 and 2 as Catalyst Precursors. We briefly examined the use of complexes **1** and **2** as catalyst precursors for the Ziegler−Natta polymerization of ethylene. Due to our inability to purify complex **3** (vide supra), we chose to exclude it from these polymerization trials. A Fisher−Porter bottle was charged with a solution of methylalumoxane (MAO) in toluene under ethylene. Separately, the complexes were dissolved in toluene and then added to the reactor, which led to an immediate color change in the solutions from light yellow to slightly orange and then to yellow within a few minutes. For both complexes, the following polymerization conditions were employed: (a) pressure of ethylene, 8.5 atm; (b) temperature, 25 and 50 °C; (c) quantity of Ru complex, 10 and 20 μmol; (d) Ru/MAO ratio, 1/1000 and 1/3000. Even at the highest temperature and concentration of reactants, only trace amounts of polymer were produced upon reaction for 1−2 h.

In these polymerization trials, the use of large excesses of MAO prevented a detailed analysis of the products formed when complexes **1** and **2** were treated with MAO. We were thus unable to determine whether any cationic alkyl complexes were formed as intermediates. In separate studies,[40] however, we have examined the reactivity of complexes **1** and **2** with $[H(Et_2O)_2][B(3,5\text{-}C_6H_3(CF_3)_2)_4]$.[41] In the presence of CO, we were able to isolate the cationic alkyl complexes, $[(\eta^6{:}\eta^1\text{-}C_6H_5CH_2CH_2PR_2)Ru(CH_3)(CO)][B(3,5\text{-}C_6H_3(CF_3)_2)_4]$ (R = Cy, Ph).[40,42] The details of these synthetic studies and an exploration of the use of the resultant cationic alkyl complexes as olefin polymerization catalysts are reported separately.

Regarding the inactivity of the cis-constrained complexes toward the polymerization of olefins, Werner has observed in similar systems ortho metalation of the phenyl moiety attached to phosphorus,[35] which would lead in our case to a Ru benzyl product that might fail to insert ethylene. Another possibility is that a stable Ru alkyl olefin complex having a high energy of insertion is formed in the reaction. The latter can plausibly occur if the olefin orients in a manner that precludes insertion (e.g., perpendicular to the alkyl group).

Conclusions

We have synthesized a new family of arene−phosphine ligands, $C_6H_5CH_2CH_2PR_2$ (R = Cy, Ph, Et), and used them to prepare the corresponding ruthenium(II) dichloride complexes, (η^6: η^1-$C_6H_5CH_2CH_2PR_2$)$RuCl_2$. Alkylation of these complexes with methyllithium afforded the novel dialkyl complexes (η^6: η^1-$C_6H_5CH_2CH_2PR_2$)$Ru(CH_3)_2$, where R = Cy (**1**), Ph (**2**), Et (**3**). Complexes **1** and **2** were thoroughly characterized by NMR spectroscopy, X-ray crystallography, and thermal

(38) We measured the ^{1}H NMR spectrum of methane in *o*-xylene-d_{10} and observed a single resonance at δ 0.43. In ^{1}H NMR spectroscopy, the singlet for ethane typically appears downfield of that for methane by ~0.6 ppm. See, for example: Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH: New York, 1993; p 52.

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(42) In contrast to ref 30, where the boron activator abstracts a methide moiety, ref 35 reports that Ph_3CX (X = PF_6^-, BF_4^-) abstracts a hydride moiety from related late-transition-metal dimethyl complexes.

stability. Due to our inability to completely purify complex **3**, we were unable to characterize it fully, nor were we able to evaluate its thermal stability. Analysis of the thermal stabilities of complexes **1** and **2** revealed that complex **1** is more stable than complex **2**; furthermore, both complexes appear to be more thermally stable than analogous nontethered systems described in the literature. Preliminary studies of the use of complexes **1** and **2** as catalyst precursors in the Ziegler−Natta polymerization of ethylene revealed that neither complex exhibited significant catalytic activity under the limited polymerization conditions examined.

Experimental Section

Materials and Methods. All solvents were dried by passage through alumina and degassed by freeze−pump−thaw methods prior to use. The compounds methyllithium and 2-(bromoethyl)benzene were purchased from Aldrich Chemical Co. and used as received. Similarly, the compounds bis(μ-chloro)bis[(*p*-cymene)chlororuthenium(II)], dicyclohexylchlorophosphine ($ClPCy_2$), diphenylchlorophosphine ($ClPPh_2$), and diethylchlorophosphine ($ClPEt_2$) were purchased from Strem Chemical Co. and used as received. All deuterated solvents were purchased from Cambridge Isotope Laboratories. Nuclear magnetic resonance (NMR) spectra were recorded on a General Electric QE-300 spectrometer operating at 300 MHz (for ^1H), 75.5 MHz (for ^{13}C), and 121 MHz (for ^{31}P). Elemental analyses were performed by National Chemical Consulting.

Synthesis of $C_6H_5CH_2CH_2PCy_2$. To a cooled (0 °C) solution of dry diethyl ether (60 mL) charged with dicyclohexylchlorophosphine (5.0 g, 2.1×10^{-2} mol) was added 1.1 equiv (9.0 mL of a 2.6 M solution; 2.4×10^{-2} mol) of $C_6H_5CH_2CH_2MgBr$ prepared by the reaction of magnesium and (2-bromoethyl)-benzene in dry diethyl ether. The solution was warmed slowly to room temperature and refluxed overnight under argon. The excess Grignard reagent was destroyed by the addition of degassed methanol, and the solution was concentrated under vacuum. Due to apparent decomposition of the product during attempted purification by column chromatography on silica gel, the crude product was used in subsequent synthetic steps (vide infra). ^1H NMR ($CDCl_3$; 300 MHz; 293 K): δ 7.26 (m, 5 H, C_6H_5), 2.73 (m, 2 H, $C_6H_5CH_2CH_2P$), 1.2−2.2 (m, 24 H, $C_6H_5CH_2CH_2P$, Cy_2).

Synthesis of $C_6H_5CH_2CH_2PPh_2$. An aliquot (25 mL, 6.8 $\times 10^{-2}$ mol) of a 2.7 M solution of $C_6H_5CH_2CH_2MgBr$ in diethyl ether was slowly added to a cooled (0 °C) solution of diphenylchlorophosphine (10 g, 4.5×10^{-2} mol) in 100 mL of dry diethyl ether. The solution was slowly warmed to room temperature and refluxed overnight under argon. The excess Grignard reagent was destroyed by the dropwise addition of 1 N HCl solution. The solution was then adjusted to basic pH by the careful addition of a saturated solution of $NaHCO_3$. The organic phase was separated, and the aqueous phase was extracted with diethyl ether (3 × 60 mL). The combined organic phases were dried over $MgSO_4$ and filtered. The volatiles were removed under vacuum, and the product was purified by column chromatography on silica gel using 40/1 hexanes/diethyl ether (R_f = 0.46, 10/1 hexanes/diethyl ether). Yield of white solid: 7.4 g, 56%.^1H NMR ($CDCl_3$; 300 MHz; 293 K): δ 7.15−7.69 (m, 15 H, *Ar*), 2.96 (m, 2 H, $C_6H_5CH_2CH_2P$), 2.59 (m, 2 H, $C_6H_5CH_2CH_2P$). $^{31}P\{^1H\}$ NMR ($CDCl_3$; 121 MHz; 293 K): δ −15.3 (s). ^{13}C NMR ($CDCl_3$; 75.5 MHz; 293 K): δ 142.68 (d, J_{CP} = 13.14 Hz, $C_6H_5CH_2CH_2P$), 138.72 (d, J_{CP} = 13.36 Hz, *Ar*), 132.91 (d, J_{CP} = 16.23 Hz, *Ar*), 132.70 (d, J_{CP} = 16.99 Hz, *Ar*), 128.56 (m, $C_6H_5CH_2CH_2P$, *Ar*), 126.08 (s, $C_6H_5CH_2CH_2P$), 32.25 (d, J_{CP} = 17.74 Hz), 30.30 (d, J_{CP} = 13.14 Hz).

Synthesis of $C_6H_5CH_2CH_2PEt_2$. This ligand was prepared using a procedure analogous to that used to prepare $C_6H_5CH_2CH_2PPh_2$, except for the use of 1.98 M $C_6H_5CH_2CH_2MgBr$ (12.16 mL, 2.4×10^{-2} mol) and diethylchlorophosphine (2.0 g, 1.6×10^{-2} mol) in dry diethyl ether (20 mL). The crude oily residue was purified by vacuum distillation. Yield: 1.00 g, 32%. ^1H NMR ($CDCl_3$; 300 MHz; 293 K): δ 7.28 (m, 5 H, C_6H_5), 2.77 (m, 2 H, $C_6H_5CH_2CH_2P$), 1.73 (m, 2 H, $C_6H_5CH_2CH_2P$), 1.48 (q, J_{HH} = 7.8 Hz, 4 H, $P(CH_2CH_3)_2$), 1.12 (m, 6 H, $P(CH_2CH_3)_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$; 121 MHz; 293 K): δ −21.3 (s). ^{13}C NMR ($CDCl_3$; 75.5 MHz; 293 K): δ 143.06, 128.34, 128.03, 125.81, 32.28 (d, J_{CP} = 14.57 Hz), 28.20 (d, J_{CP} = 15.55 Hz), 18.64 (d, J_{CP} = 11.33 Hz), 9.50 (d, J_{CP} = 11.78 Hz).

Synthesis of (*p*-cymene)$Ru(PCy_2CH_2CH_2C_6H_5)Cl_2$. The synthesis was performed using an adaptation of a related literature procedure.[33] An aliquot of [(*p*-cymene)$RuCl_2]_2$ (3.14 g, 5.13×10^{-3} mol) was dissolved in 80 mL of benzene. To this solution was added 2.5 equiv of crude $C_6H_5CH_2CH_2PCy_2$ prepared as described above (*note:* the amount of $C_6H_5CH_2CH_2PCy_2$ was estimated by integration using ^1H NMR spectroscopy). The solvent was evaporated, and the resultant red residue was extracted into CH_2Cl_2 and the extract filtered. The solution was evaporated to dryness, and the resultant red solid was washed with hexanes and diethyl ether and then dried under vacuum. Yield: 4.63 g, 75%.^1H NMR ($CDCl_3$; 300 MHz; 293 K): δ 5.55 (s, 4 H, η^6-$CH_3C_6H_4CH(CH_3)_2$), 2.82 (m, 2 H, $C_6H_5CH_2CH_2P$), 2.29 (m, 2 H, $C_6H_5CH_2CH_2P$), 2.10 (s, 3 H, Ar−CH_3), 1.40−2.03 (m, 23 H, Cy_2, $CH(CH_3)_2$), 1.28 (d, J_{HH} = 6.9 Hz, 6 H, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2; 121 MHz; 293 K): δ 25.5 (s). ^{13}C NMR ($CDCl_3$; 75.5 MHz; 293 K): δ 141.65 (*Ar)*, 128,56 (m, *Ar)*, 126.10 (*Ar)*, 108.69 (η^6-$CH_3C_6H_4CH(CH_3)_2$), 94.11 (η^6-$CH_3C_6H_4CH(CH_3)_2$), 88.94 (η^6-$CH_3C_6H_4CH(CH_3)_2$), 83.66 (η^6-$CH_3C_6H_4CH(CH_3)_2$), 37.88 (d, J_{CP} = 20.5 Hz), 31.10 (d, J_{CP} = 5.1 Hz), 30.89, 29.45, 29.07, 27.74, 26.72, 22.55, 18.21. A satisfactory analysis could not be obtained. Anal. Calcd for $C_{30}H_{45}RuPCl_2$: C, 59.20; H, 7.40. Found: C, 58.43; H, 7.28.

Synthesis of (*p*-cymene)$Ru(PPh_2CH_2CH_2C_6H_5)Cl_2$. An aliquot of [(*p*-cymene)$RuCl_2]_2$ (1.00 g, 1.63×10^{-3} mol) was dissolved in 50 mL of benzene. To this solution was added 2.1 equiv of $C_6H_5CH_2CH_2PPh_2$ (0.99 g, 3.4×10^{-3} mol). The solution was heated at 45 °C for 3 h, and then the solvent was removed by evaporation. The resultant red residue was extracted into CH_2Cl_2, and the extract was filtered and evaporated to dryness. The resultant red solid was washed with hexanes and diethyl ether, and then dried under vacuum. Yield: 1.85 g, 95%. ^1H NMR ($CDCl_3$; 300 MHz; 293 K): δ 7.94 (m, 4 H, PPh_2), 7.53 (m, 6 H, PPh_2), 7.13 (m, 3 H, C_6H_5), 6.93 (m, 2 H, C_6H_5), 5.26 (d, J_{HH} = 6.3 Hz, 2 H, η^6-$CH_3C_6H_4CH(CH_3)_2$, 5.09 (d, J_{HH} = 6.3 Hz, 2 H, η^6-$CH_3C_6H_4CH(CH_3)_2$, 2.85 (m, 2 H, $C_6H_5CH_2CH_2P$), 2.55 (m, 1 H, $CH(CH_3)_2$), 2.32 (m, 2 H, $C_6H_5CH_2CH_2P$), 1.90 (s, 3 H, Ar−CH_3), 0.83 (d, J_{HH} = 6.9 Hz, 6 H, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$; 121 MHz; 293 K): δ 23.4 (s). ^{13}C NMR ($CDCl_3$; 75.5 MHz; 293 K): δ 141.65 (d, J_{CP} = 12.16 Hz, *Ar*), 133.40 (d, J_{CP} = 8.23 Hz, *Ph2*), 133.28 (m, *Ph2*), 130.83 (*Ph2*), 128.35 (m, *Ar*), 126.02 (*Ar*), 108.39 (η^6-$CH_3C_6H_4CH(CH_3)_2$), 93.94 (η^6-$CH_3C_6H_4CH(CH_3)_2$), 90.65 (η^6-$CH_3C_6H_4CH(CH_3)_2$), 85.80 (η^6-$CH_3C_6H_4CH(CH_3)_2$), 30.15, 29.68, 25.19 (d, J_{CP} = 26.27 Hz), 21.48, 17.53. Anal. Calcd for $C_{30}H_{33}RuPCl_2$: C, 60.40; H, 5.54. Found: C, 60.65; H, 5.40.

Synthesis of (*p*-cymene)$Ru(PEt_2CH_2CH_2C_6H_5)Cl_2$. An aliquot of [(*p*-cymene)$RuCl_2]_2$ (0.50 g, 8.2×10^{-4} mol) was dissolved in 50 mL of benzene. To this solution was added 2.3 equiv of $C_6H_5CH_2CH_2PEt_2$ (0.36 g, 1.9×10^{-3}). The solution was refluxed for 30 min, and the solvent was evaporated to afford a red residue, which was extracted into CH_2Cl_2, filtered, and evaporated to dryness. The resultant red solid was washed with hexanes and diethyl ether and then dried under vacuum. Yield: 0.78 g, 95%.^1H NMR ($CDCl_3$; 300 MHz; 293 K): δ 7.27 (m, 5 H, C_6H_5), 5.45 (m, 4 H, η^6-$CH_3C_6H_4CH(CH_3)_2$), 2.85 (m, 3 H, $CH(CH_3)_2$, $C_6H_5CH_2CH_2P$), 2.26 (m, 2 H, $C_6H_5CH_2CH_2P$), 2.17 (m, 4 H, $P(CH_2CH_3)_2$), 2.11 (s, 3 H, Ar−CH_3), 1.26 (d, J_{HH} = 6.9 Hz, 6 H, $CH(CH_3)_2$), 1.17 (m, 6 H, $P(CH_2CH_3)_2$). $^{31}P\{^1H\}$

NMR ($CDCl_3$; 121 MHz; 293 K): δ 21.2 (s). ^{13}C NMR ($CDCl_3$; 75.5 MHz; 293 K): δ 142.12 (d, J_{CP} = 12.30 Hz, *Ar*), 128.74 (*Ar*), 128.17 (*Ar*), 126.36 (*Ar*), 107.54 (η^6-$CH_3C_6H_4CH(CH_3)_2$), 94.59 (η^6-$CH_3C_6H_4CH(CH_3)_2$), 88.99 (η^6-$CH_3C_6H_4CH(CH_3)_2$), 84.86 (η^6-$CH_3C_6H_4CH(CH_3)_2$), 30.75, 29.93, 26.98 (d, J_{CP} = 24.23 Hz), 22.40, 18.38, 18.21 (d, J_{CP} = 25.82 Hz), 7.99 (d, J_{CP} = 6.88 Hz). Anal. Calcd for $C_{22}H_{33}RuPCl_2$: C, 52.80; H, 6.60. Found: C, 52.43; H, 6.47.

Synthesis of (η^6:η^1-$C_6H_5CH_2CH_2PCy_2$)$RuCl_2$. A sample of 4.63 g (7.61×10^{-3} mol) of (*p*-cymene)Ru($PCy_2CH_2CH_2C_6H_5$)-Cl_2 was refluxed in 80 mL of degassed chlorobenzene for 6 h under argon. Fine orange crystals, which formed during the reaction, were isolated by filtration and washed with hexanes and diethyl ether. The remaining solution was again refluxed, and the crystals were collected. This process was repeated three times until crystal formation was observed to cease. The crystals were washed with hexanes and diethyl ether and dried under vacuum. Yield: 3.40 g, 94%. ^1H NMR ($CDCl_3$; 300 MHz; 293 K): δ 6.22 (td, J_{HH} = 5.7 Hz, J_{HH} = 2.4 Hz, 1 H, η^6-C_6H_5), 5.84 (t, J_{HH} = 5.7 Hz, 2 H, η^6-C_6H_5), 5.01 (d, J_{HH} = 5.7 Hz, 2 H, η^6-C_6H_5), 2.92 (m, 2 H, $C_6H_5CH_2CH_2$P), 2.63 (dt, J_{HH} = 7.5 Hz, J_{gem} = 18.6 Hz, 2 H, $C_6H_5CH_2CH_2$P), 2.27 (m, 2 H, Cy_2), 1.28−1.83 (m, 20 H, Cy_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$; 121 MHz; 293 K): δ 70.2 (s). ^{13}C NMR ($CDCl_3$; 75.5 MHz; 293 K): δ 112.00 (η^6-C_6H_5), 97.66 (η^6-C_6H_5), 90.88 (η^6-C_6H_5), 75.25 (η^6-C_6H_5), 34.67 (d, J_{CP} = 26.7 Hz), 34.15 (d, J_{CP} = 21.3 Hz), 32.07, 26.06−27.53 (m). Anal. Calcd for $C_{20}H_{32}RuPCl_2$: C, 50.53; H, 6.74. Found: C, 50.66; H, 6.81.

Synthesis of (η^6:η^1-$C_6H_5CH_2CH_2PPh_2$)$RuCl_2$. A sample of 2.2 g (3.7×10^{-3} mol) of (*p*-cymene)Ru($PPh_2CH_2CH_2C_6H_5$)-Cl_2 was refluxed in 50 mL of degassed chlorobenzene for 24 h under argon. The solvent was removed under vacuum, and the reddish brown residue was washed with hexane, diethyl ether, and cold CH_2Cl_2. The compound was recrystallized from CH_2-Cl_2/diethyl ether. Yield: 1.06 g, 62%. ^1H NMR ($CDCl_3$; 300 MHz; 293 K): δ 7.75 (m, 4 H, PPh_2), 7.40 (m, 6 H, PPh_2), 6.25 (td, J_{HH} = 5.7 Hz, J_{HH} = 2.4 Hz, 1 H, η^6-C_6H_5), 6.05 (t, J_{HH} = 5.7 Hz, 2 H, η^6-C_6H_5), 4.50 (d, J_{HH} = 5.7 Hz, 2 H, η^6-C_6H_5), 3.55 (m, 2 H, $C_6H_5CH_2CH_2$P), 2.64 (dt, J_{HH} = 7.2 Hz, J_{gem} = 20.4 Hz, 2 H, $C_6H_5CH_2CH_2$P). $^{31}P\{^1H\}$ NMR ($CDCl_3$; 121 MHz; 293 K): δ 46.8 (s). ^{13}C NMR ($CDCl_3$; 75.5 MHz; 293 K): δ 133.55 (PPh_2), 131.99 (PPh_2), 131.29 (PPh_2), 128.84 (PPh_2), 112.39 (η^6-C_6H_5), 98.65 (η^6-C_6H_5), 88.52 (η^6-C_6H_5), 79.81 (η^6-C_6H_5), 44.83 (d, J_{CP} = 33.3 Hz), 28.41. Anal. Calcd for $C_{20}H_{19}$-$RuPCl_2$: C, 51.95; H, 4.11. Found: C, 52.26; H, 3.88.

Synthesis of (η^6:η^1-$C_6H_5CH_2CH_2PEt_2$)$RuCl_2$. A sample of 0.5 g (1×10^{-3} mol) of (*p*-cymene)Ru($PEt_2CH_2CH_2C_6H_5$)Cl_2 was refluxed in 50 mL of degassed chlorobenzene for 16 h under argon. The solvent was removed under vacuum, and the reddish brown residue was washed with hexane and diethyl ether. The compound was recrystallized from CH_2Cl_2/diethyl ether. Yield: 0.29 g, 80%.^1H NMR ($CDCl_3$; 300 MHz; 293 K): δ 6.23 (td, J_{HH} = 5.7 Hz, J_{HH} = 2.4 Hz, 1 H, η^6-C_6H_5), 5.89 (t, J_{HH} = 5.7 Hz, 2 H, η^6-C_6H_5), 4.90 (d, J_{HH} = 5.7 Hz, 2 H, η^6-C_6H_5), 2.98 (m, 2 H, $C_6H_5CH_2CH_2$P), 2.68 (dt, J_{HH} = 7.2 Hz, J_{gem} = 20.4 Hz, 2 H, $C_6H_5CH_2CH_2$P), 2.05 (m, 4 H, P(CH_2-CH_3)$_2$), 1.19 (m, 6 H, P(CH_2CH_3)$_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2; 121 MHz; 293 K): δ 63.7 (s). ^{13}C NMR ($CDCl_3$; 75.5 MHz; 293 K): δ 112.32 (η^6-C_6H_5), 98.86 (η^6-C_6H_5), 88.58 (η^6-C_6H_5), 75.32 (η^6-C_6H_5), 38.69 (d, J_{CP} = 29.46 Hz), 30.49, 18.17 (d, J_{CP} = 26.50 Hz), 7.99. Anal. Calcd for $C_{12}H_{19}RuPCl_2$: C, 39.34; H, 5.19. Found: C, 39.20; H, 5.04.

Synthesis of (η^6:η^1-$C_6H_5CH_2CH_2PCy_2$)$Ru(CH_3)_2$ (1). The corresponding dichloride, (η^6: η^1-$C_6H_5CH_2CH_2PCy_2$)$RuCl_2$ (0.50 g, 1.1×10^{-4} mol), was suspended in 20 mL of dry diethyl ether. To the above solution was added 6.2 equiv of methyllithium (6.8×10^{-3} mol) at −78 °C. The solution was gradually warmed to room temperature and stirred for 1 h. The solvent was evaporated, and the residue was extracted with benzene. The brown solid obtained after evaporation of the benzene was purified by column chromatography on particulate Al_2O_3 using diethyl ether as the eluant. The yellow fractions were collected and subjected to slow evaporation of the diethyl ether to afford yellow crystals of **1**. Yield: 0.17 g, 37%.^1H NMR (CD_2Cl_2; 300 MHz; 293 K): δ 5.13 (t, J_{HH} = 5.7 Hz, 2 H, η^6-C_6H_5), 4.97 (d, J_{HH} = 5.7 Hz, 2 H, η^6-C_6H_5), 4.53 (t, J_{HH} = 5.7 Hz, 1 H, η^6-C_6H_5), 2.46 (m, 2 H, $C_6H_5CH_2CH_2$P), 2.10 (dt, J_{HH} = 7.5 Hz, J_{gem} = 16.5 Hz, 2 H, $C_6H_5CH_2CH_2$P), 1.20−1.78 (m, 22 H, Cy_2), −0.02 (d, J_{HP} = 4.8 Hz, 6 H, Ru(CH_3)$_2$). $^{31}P\{^1H\}$ NMR (CD_2-Cl_2; 121 MHz; 293 K): δ 64.4 (s). ^{13}C NMR (CD_2Cl_2; 75.5 MHz; 293 K): δ 110.65 (d, J_{CP} = 3.39 Hz, η^6-C_6H_5), 96.53 (d, J_{CP} = 3.02 Hz, η^6-C_6H_5), 82.21 (η^6-C_6H_5), 78.54 (d, J_{CP} = 13.8 Hz, η^6-C_6H_5), 39.12 (d, J_{CP} = 25.3 Hz), 34.00 (d, J_{CP} = 17.7 Hz), 31.36 (d, J_{CP} = 6.6 Hz), 28.40, 28.07 (d, J_{CP} = 11.48 Hz), 27.78 (d, J_{CP} = 9.06 Hz), 27.53, 27.13, −12.67 (d, J_{CP} = 15.7 Hz). A satisfactory analysis could not be obtained. Anal. Calcd for $C_{22}H_{38}RuP$: C, 60.83; H, 8.75. Found: C, 61.31; H, 8.48.

Synthesis of (η^6:η^1-$C_6H_5CH_2CH_2PPh_2$)$Ru(CH_3)_2$ (2). The synthesis of compound **2** was performed using a procedure analogous to that used to prepare compound **1**. Yellow crystals of **2** were obtained by the slow evaporation of CH_2Cl_2. Yield: 48%.^1H NMR (CD_2Cl_2; 300 MHz; 293 K): δ 7.36 (m, 10 H, PPh_2), 5.42 (t, J_{HH} = 5.7 Hz, 2 H, η^6-C_6H_5), 5.10 (d, J_{HH} = 5.7 Hz, 2 H, η^6-C_6H_5), 4.87 (t, J_{HH} = 5.7 Hz, 1 H, η^6-C_6H_5), 2.96 (m, 2 H, $C_6H_5CH_2CH_2$P), 2.11 (dt, J_{HH} = 7.2 Hz, J_{gem} = 21.9 Hz, 2 H, $C_6H_5CH_2CH_2$P), −0.19 (d, J_{HP} = 6.0 Hz, 6 H, Ru-(CH_3)$_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2; 121 MHz; 293 K): δ 63.7 (s). ^{13}C NMR (CD_2Cl_2; 75.5 MHz; 293 K): δ 135.24 (d, J_{CP} = 34.88 Hz, Ph_2), 133.36 (d, J_{CP} = 9.66 Hz, Ph_2), 129.67, 128.38 (d, J_{CP} = 9.21 Hz, Ph_2), 108.46 (η^6-C_6H_5), 98.97 (η^6-C_6H_5), 84.87 (η^6-C_6H_5), 76.68 (d, J_{CP} = 15.2 Hz, (η^6-C_6H_5), 47.48 (d, J_{CP} = 30.9 Hz), 28.64 (d, J_{CP} = 7.5 Hz), −10.82 (d, J_{CP} = 16 Hz). Anal. Calcd for $C_{22}H_{25}RuP$: C, 62.71; H, 5.94. Found: C, 62.87; H, 5.98.

Synthesis of (η^6:η^1-$C_6H_5CH_2CH_2PEt_2$)$Ru(CH_3)_2$ (3). The corresponding dichloride, (η^6: η^1-$C_6H_5CH_2CH_2PEt_2$)$RuCl_2$ (0.123 g, 3.34×10^{-4} mol), was suspended in 20 mL of diethyl ether. To the above solution was added 5 equiv of methyllithium (1.69×10^{-3} mol) at −78 °C. The solution was gradually warmed to

Table 3. Crystal Data and Structure Refinement Details for 1

compd	$Me_2RuPh(CH_2)_2P(C_6H_{11})_2$
empirical formula	$C_{22}H_{37}PRu$
fw	433.56
temp	243 K
wavelength	0.710 73 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	
a	8.1930(1) Å
b	8.334(1) Å
c	15.904(3) Å
α	98.95(3)°
β	98.77(3)°
γ	102.76(3)°
V	1026.4(3) Å^3
Z	2
density (calcd)	1.403 g/mL
abs coeff	0.843 mm^{-1}
F(000)	456
cryst size	0.3 × 0.3 × 0.2 mm
θ range for data collecn	2.56−27.49°
limiting indices	$-10 < h < 10$, $0 < k < 8$, $-20 < l < 20$
no. of rflns collected	3159
no. of indep rflns	2831 (R_{int} = 0.0181)
abs cor	ψ scans
max and min transmissn	1.0000 and 0.6824
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	2822/6/239
goodness of fit on F^2	1.041
final R indices ($I > 4\sigma(I)$)	R1 = 0.0332, wR2 = 0.0916
R indices (all data)	R1 = 0.0365, wR2 = 0.0952
largest diff peak and hole	0.605 and −0.554 e/Å^3

Table 4. Crystal Data and Structure Refinement for 2

compd	$Me_2RuPh(CH_2)_2P(C_6H_5)_2$
empirical formula	$C_{22}H_{25}PRu$
fw	421.46
temp	213 K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	$P2_1/n$
unit cell dimens	
a	11.210(2) Å
b	14.089(3) Å
c	12.143(2) Å
α	90°
β	98.02(3)°
γ	90°
V	1899.1(6) Å^3
Z	4
density (calcd)	1.474 g/mL
abd coeff	0.910 mm^{-1}
F(000)	864
cryst size	0.40 × 0.35 × 0.30 mm
θ range for data collecn	2.23−27.50°
limiting indices	$0 < h < 12$, $0 < k < 18$, $-15 < l < 15$
no. of rflns collected	3345
no. of indep rflns	3130 ($R_{int} = 0.0448$)
abs cor	*ψ* scans
max and min transmissn	1.0000 and 0.9076
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	3129/0/219
goodness of fit on F^2	1.089
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0328, wR2 = 0.0949
R indices (all data)	R1 = 0.0432, wR2 = 0.0998
largest diff peak and hole	0.834 and −0.430 e/Å^3

room temperature and stirred for 1 h. The solvent was evaporated, and the residue was extracted with benzene. The brown solid obtained after evaporation of benzene was subjected to column chromatography on particulate Al_2O_3 using diethyl ether as the eluant. A yellow solution was collected, which turned brown during evaporation of the diethyl ether. The apparent decomposition precluded the isolation of the pure samples of **3**. ^{1}H NMR (C_6D_6; 300 MHz; 293 K): δ 5.04 (t, J_{HH} = 5.7 Hz, 2 H, η^6-C_6H_5), 4.65 (t, J_{HH} = 5.7 Hz, 1 H, η^6-C_6H_5), 4.53 (d, J_{HH} = 5.7 Hz, 2 H, η^6-C_6H_5), 1.87 (m, 2 H, C_6H_5-CH_2CH_2P), 1.60 (dt, J_{HH} = 7.5 Hz, J_{gem} = 18.0 Hz, 2 H, $C_6H_5CH_2CH_2$P), 1.34 (m, 4 H, P(CH_2CH_3)$_2$), 0.81 (m, 6 H, P(CH_2CH_3)$_2$), 0.50 (d, J_{HP} = 5.7 Hz, 6 H, Ru(CH_3)$_2$).

X-ray Crystal Structure Determinations. The data were collected using the TEXSAN[43] automatic data collection series on a Rigaku AFC5S diffractometer. The crystallographic data collection parameters for compounds **1** and **2** are summarized in Tables 3 and 4, respectively. The data were corrected for Lorentz and polarization effects and for absorption correction using *ψ* scans. Crystal and instrument stability were checked by measuring 3 standard reflections every 150 observations. Structures were solved using SHELXS-97[44] on a PC. Weighted *R* factors (R_w) and all goodness of fit values (*S*) were based on F^2; conventional *R* factors (*R*) were based on *F*. The H atom positions were refined using a riding model.

Trial Polymerizations of Ethylene Using MAO-Activated 1 and 2.[45] These experiments were performed in a Fisher−Porter bottle equipped with a pressure release valve, a sample injection inlet, an ethylene and argon inlet, and a pressure gauge. In a typical polymerization trial, a mixture of MAO (1000−3000 equiv based on Ru) and toluene (30 mL) were placed in the Fisher−Porter bottle, which was then pressurized with ethylene at 40 psi for 5 min. The pressure of ethylene was slowly reduced to 25 psi, and a solution containing the ruthenium complexes (10 or 20 *μ*mol) was injected by syringe under a flow of ethylene. The reactor was pressurized with ethylene (8.5 atm), and the reaction mixture was stirred for 1−2 h at temperatures adjusted to either 25 or 50 °C over several independent runs. The reaction mixture was then slowly poured into a methanolic solution containing 5% HCl to precipitate any polyethylene formed in the reaction.

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Supporting Information Available: Tables giving X-ray crystallographic data for complexes **1** and **2** and figures giving ^{1}H NMR spectra for complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0300070

(43) Molecular Structure Corporation Single-Crystal Structure Analysis Software (1995b); MSC, 3200 Research Forest Drive, The Woodlands, TX 77381.

(44) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(45) The polymerization apparatus and reagents were examined for possible contamination through control experiments using Cp_2ZrHCl as the catalyst precursor. In these experiments, ample amounts of polyethylene were produced.