

Organometallic Macrocyclic Chemistry. 6.¹ Chelate-Assisted Macrocyclization of 4,7,10-Trithiatrideca-2,11-diyne

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The diyne 4,7,10-trithiatrideca-2,11-diyne (TTDD) reacts smoothly at room temperature with $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ to form $[\text{Ru}(\text{CO})(\text{PPh}_3)\{\eta^4\text{-S}(\text{C}_2\text{H}_4\text{SCCMe})_2\text{CO-}\kappa\text{S}\}]$, a cyclopentadienone complex in which the unique sulfur atom is also coordinated to the metal but may be displaced by dppe to provide $[\text{Ru}(\text{CO})(\text{dppe})\{\eta^4\text{-S}(\text{C}_2\text{H}_4\text{SCCMe})_2\text{CO}\}]$. In contrast, 2,8-decadiyne fails to cyclize even at elevated temperatures, implicating thioether coordination in the mechanism of TTDD macrocyclization.

Introduction

A range of ruthenium complexes have been shown to couple alkynes.² The various products include examples of ruthenacyclopentadienes,³ cyclobutadiene complexes,⁴ enynes in the case of terminal alkynes,⁵ and either free arenes or their complexes.⁶ For substrates bearing carbonyl ligands, the possibility of CO incorporation arises, leading to cyclopentadienone or quinone formation,^{7–9} including polymetallic examples.¹⁰ With this plethora of possibilities in mind, we are investigating the organometallic chemistry of 4,7,10-trithiatrideca-2,11-diyne (TTDD) with ruthenium complexes, in the hope that new routes to functionalized thioether macrocycles might be developed.

The complex $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ has been shown to react cleanly with diphenylacetylene or diphenylbutadiyne to provide the simple adducts $[\text{Ru}(\eta^2\text{-PhC}\equiv\text{CR})(\text{CO})_2(\text{PPh}_3)_2]$ ($\text{R} = \text{Ph}$ (**1a**),¹¹ $\text{C}\equiv\text{CPh}$ (**1b**)¹²). In these reactions, which proceed under ambient conditions, no further coordination or coupling of the alkynes ensues, although complexes **1** appear plausible through unrec-

ognized intermediates in the alkyne coupling reactions mediated by $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ in refluxing toluene, curiously under an atmosphere of CO_2 .⁹ Herein we report the reaction of TTDD with $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$, which does indeed provide access to a novel polythia-macrocyclic via $[2 + 2 + 1]$ macrocyclization of the α,ω -diyne with coordinated CO.

Results and Discussion

Synthesis. Addition of benzene or toluene to an equimolar mixture of TTDD and $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ at room temperature results in the precipitation of a crystalline product. The complex is a bright yellow, air-stable solid, poorly soluble in aliphatic and aromatic solvents but with reasonable solubility in halogenated solvents and ethanol. It is formulated as $[\text{Ru}(\text{CO})(\text{PPh}_3)\{\eta^4\text{-S}(\text{C}_2\text{H}_4\text{SCCMe})_2\text{CO-}\kappa\text{S}\}]$ (**2**) on the basis of spectroscopic data and X-ray crystallography. The triclinic crystal chosen for study was twinned, and the new refinement procedures are described later in this paper. An alternative and more expedient synthesis of **2** was also developed via the reaction of $[\text{RuHCl}(\text{CO})_2(\text{PPh}_3)_2]$ with TTDD in the presence of DBU, avoiding the need to isolate $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$.¹³ The complex **2** is also formed from the reaction of $[\text{Ru}(\text{CO})_3(\text{PPh}_3)_2]$ with TTDD, but only under forcing conditions (refluxing toluene).

The molecular geometry of the chiral complex **2** is depicted in Figure 1 and comprises a cyclopentadienone coordinated to ruthenium(0), to which are also coordinated one carbonyl ligand and one triphenylphosphine ligand. The cyclopentadienone arises from the regioselective $[2 + 2 + 1]$ macrocyclization of the α,ω -diyne with

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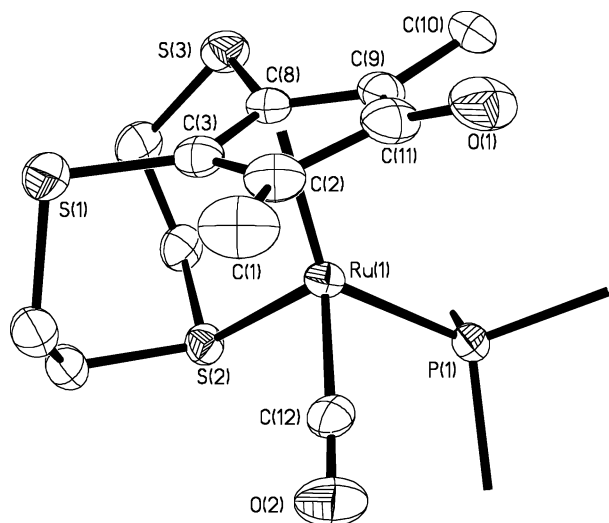
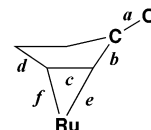


Figure 1. ORTEP diagram (50% probability ellipsoids) of **2** (hydrogen atoms and phenyl rings omitted). Selected bond distances (Å) and angles (deg): Ru1–S2 = 2.377(1), Ru1–P1 = 2.342(1), Ru1–C2 = 2.239(6), Ru1–C3 = 2.171(6), Ru1–C8 = 2.210(6), Ru1–C9 = 2.325(6), Ru1–C11 = 2.492(6), Ru1–C12 = 1.854(7), C2–C3 = 1.433(8), C2–C11 = 1.453(9), C3–C8 = 1.459(8), C8–C9 = 1.420(7), C9–C11 = 1.471(9), C11–O1 = 1.250(7), C12–O2 = 1.159(7); P1–Ru1–S2 = 91.5(1), P1–Ru1–C12 = 88.5(2), S2–Ru1–C12 = 96.2(2).

carbon monoxide, such that a nine-membered trithia-macrocycle is annulated to the cyclopentadienone. Mononuclear ruthenium(0) thioether complexes have yet to be structurally characterized; however, polynuclear ruthenium(0) carbonyl adducts of cyclic thioethers typically display Ru–S separations of 2.306–2.409 Å.^{14–16} Thus, the bond between ruthenium and the unique sulfur of the macrocycle (Ru1–S2 at 2.377(1) Å) appears unremarkable, as do the bond lengths between ruthenium and the carbonyl and phosphine ligands. The geometric parameters of interest are associated with the η^4 -cyclopentadienone ligand. However, to date there do not appear to exist any structural data for either free or complexed chalcogen-substituted cyclopentadienones. A wealth of data exists for nonfunctionalized cyclopentadienone complexes of both ruthenium(0) and ruthenium(II). From these, the general pattern emerges that η^4 coordination results in a loss of the localized single and double bonding apparent in free cyclopentadienones, while the geometric parameters associated with the (noncoordinated) ketone remain essentially unchanged. This is illustrated in Table 1 with reference to the crystal structures of (PhC)₄CO (**3**),¹⁷ [Ru⁰{ η^4 -(PhC)₄CO}(CO)₃] (**4**),¹⁸ [Ru^{II}{ η^4 -(HC)₄CO}Br(η -C₅H₅)] (**5**),¹⁹ and **2**. The oxidation state of the ruthenium appears not to affect geometric parameters within the

Table 1. Comparative Geometric Parameters (Å) for (PhC)₄CO (3**),¹⁷ [Ru⁰{ η^4 -(PhC)₄CO}(CO)₃] (**4**),¹⁸ [Ru^{II}{ η^4 -(HC)₄CO}Br(η -C₅H₅)] (**5**),¹⁹ and **2**^a**



	3	4	5	2
<i>a</i>	1.211	1.224	1.22	1.250
<i>b</i>	1.502	1.488	1.49	1.462
<i>c</i>	1.350	1.447	1.42	1.427
<i>d</i>	1.521	1.437	1.46	1.459
<i>e</i>		2.228	2.263	2.282
<i>f</i>		2.213	2.167	2.191

^a The parameters *b*, *c*, *e*, and *f* are the average of two values.

ring significantly (**4** vs **5**). Consideration of these data suggests that the inclusion of the cyclopentadienone of **2** within a chelated cyclic structure (involving two π -donative thiolate substituents) does not lead to significant changes in the geometry or indeed the orientation (tilting) of the ring.

The ¹H NMR spectrum of **2** (CD₂Cl₂) reflects the chirality of the complex, with eight well-separated multiplets being observed over the range δ 1.11–4.10, corresponding to each of the eight chemically inequivalent S(C₂H₂)₂ proton environments (see the Supporting Information for COSY (¹H, ¹H) and HMQC (C–H correlation) spectra). In the ¹³C{¹H} NMR spectrum, the metal carbonyl appears at δ 208.3 (br, *cis*-²J(PC) not resolved), while the ketonic carbonyl is observed at δ 155.0. The two carbonyl environments are also reflected in the infrared spectrum of **2**, with ν_{CO} for the metal carbonyl observed at 1929 cm⁻¹ and the ketonic carbonyl at 1561 cm⁻¹ (CH₂Cl₂).

A mechanism for the formation of **2** is suggested in Scheme 1. This involves initial loss of a phosphine ligand, with coordination of one of the triple bonds of TTDD, akin to the reactions of [Ru(CO)₂(PPh₃)₃] with PhC≡CR (R = Ph, C≡CPh).^{11,12} Coupling of the coordinated alkyne with carbon monoxide and dissociation of either a phosphine or hemilabile thioether donor^{20–22} allows coordination of the second alkynyl group, and insertion of this linkage into the vinylic bond of the metallacycle with ultimate reductive elimination provides the cyclopentadienone. The specific order of events remains conjecture; however, a similar process was inferred from the reactions of [Os(CO)₅] with alkynes.⁸ More definitive support comes from Roper's observation that [Os(CO)(CS)(PPh₃)₃] reacts with diphenylacetylene or ethyne to provide an osmacyclobutenethione²⁰ or an osmacyclohexadienethione ("osmabenzene," Scheme 2), respectively.²³

To investigate the assertion that thioether coordination plays a role, 2,8-decadiyne was treated with [Ru-

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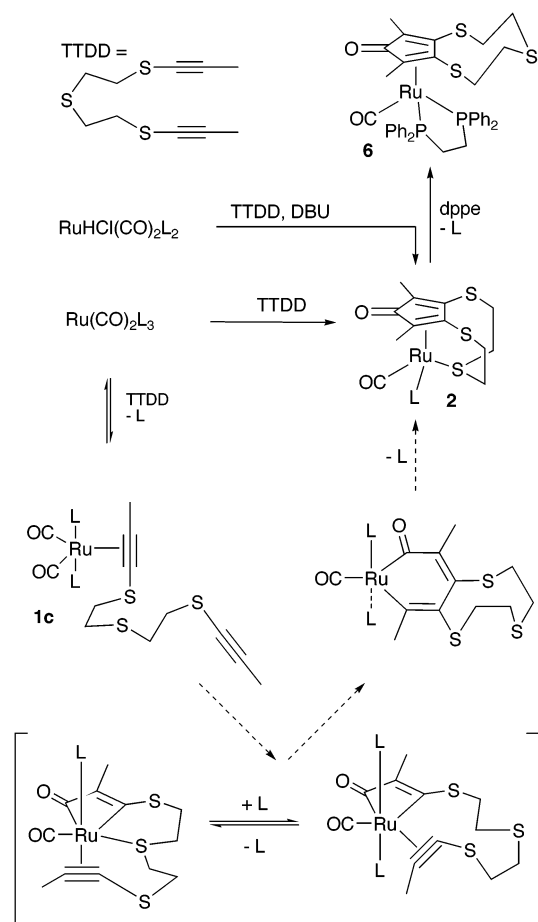
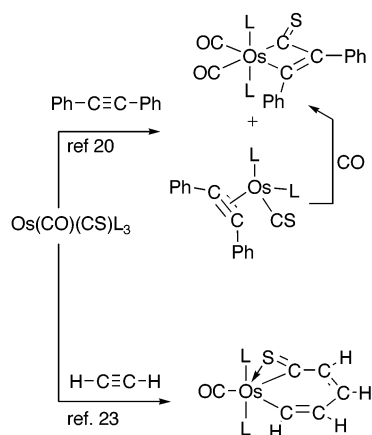
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Scheme 1. Synthesis and Suggested Mechanism for the Formation of 2 (L = PPh₃)

Scheme 2. Model Compounds Relevant to Cyclopentadienone Formation (L = PPh₃)^{20,23}


(η -C₂H₄)(CO)₂(PPh₃)₂].¹¹ This complex serves as an alternative synthetic equivalent of “Ru(CO)₂(PPh₃)₂” but offers two advantages. First, it is more soluble (for in situ spectroscopic monitoring), but more importantly, the reactions of [Ru(CO)₂(PPh₃)₃] with simple aliphatic alkynes do not proceed to completion, due to competition between the alkyne and liberated PPh₃. Under conditions analogous to those used for the synthesis of **2**, addition of 2 equiv of 2,8-decadiyne to a C₆D₆ solution of [Ru(η -C₂H₄)(CO)₂(PPh₃)₂] led to a new resonance in the ³¹P{¹H} NMR spectrum at δ 48.2, corresponding to the simple alkyne adduct, observed in a 1:2 ratio with

the starting ethylene complex. Heating the mixture led to the disappearance of this resonance and the production of a variety of products, including [Ru(CO)₂(PPh₃)₃], [Ru(CO)₃(PPh₃)₂], and PPh₃ as well as unreacted starting material and several uncharacterized products. Similar results were obtained when the reaction was carried out in the presence of tetrahydrothiophene. Thus, the inclusion of *intramolecular* thioether donors clearly plays a crucial role in the macrocyclization leading to **2**.

Thioether coordination to ruthenium(0) might be expected to be weak. Accordingly, **2** was treated with 1,2-bis(diphenylphosphino)ethane (dppe) in refluxing toluene. This led to gradual dissolution of **2** concomitant with the formation of [Ru{ η ⁴-S(C₂H₄SCCMe)₂CO}(CO)(dppe)] (**6**) as a pale yellow solid (Scheme 1). The comparative simplicity and chemical shift range of the S(C₂H₄)₂ component of the ¹H NMR spectrum relative to **2** suggests that the unique sulfur atom is no longer coordinated to the ruthenium center. Thus, the pendant macrocycle and the bidentate dppe ligand straddle a molecular plane of symmetry, a premise further supported by the appearance of a single resonance (δ 60.5) in the ³¹P{¹H} NMR spectrum of **6** and a single methyl resonance in both the ¹H and ¹³C{¹H} NMR spectra (δ 1.62 and 9.2, respectively). Notably, the formation of [Ru(CO)(dppe)₂]²⁴ was not observed in this reaction, indicating that the cyclopentadienone coordination was not labile.

The reactions of **2** with a variety of other small molecules were investigated. At room temperature in CH₂Cl₂, **2** does not react with NEt₃, TTDD, or CO; it also does not react with CNC₆H₃Me₂-2,6 in refluxing toluene or with MeLi in diethyl ether at room temperature. With bromine or AgPF₆, reactions occur at room temperature (CH₂Cl₂), providing, however, thus far intractable mixtures. Unfortunately, for the present system the prospect of including this [2 + 2 + 1] macrocyclization within a catalytic synthesis is untenable due to (i) the rapid and irreversible reaction of [Ru(CO)₂(PPh₃)₃] with CO to provide substitution-inert [Ru(CO)₃(PPh₃)₂] and (ii) the failure of the product **2** to react with CO or TTDD to liberate the desired macrocycle. However, these are factors peculiar to this particular zerovalent ruthenium system and it may be hoped that the key steps demonstrated here may be extendable to other, more potentially labile, metal centers.

Crystal Structure Solution. The constrained least-squares refinement program RAELS2000 was used for refinement.²⁵ As detailed elsewhere,²⁶ this program allows twin parameters a_i in the model $Y(\mathbf{h}) = \sum_j a_j F(\mathbf{h}_j)$ to be modified to become $a_j p_j$, where p_j is a refinable parameter and j is an integer included on the reflection file ($p_j = 1.0$ if $j = 0$). In an undistorted reciprocal space, the spacing between twin-related spots is in the direction of \mathbf{c}^* . Procedures for the optimization of data collection select a strategy that tends to have \mathbf{c}^* roughly parallel to the plane of the CCD plate. This had the

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fortuitous consequence that, in the data collection, the separation of reflections overlapped because of twinning was reasonably constant for any particular separation along \mathbf{c}^* . The twin plane is an n glide perpendicular to \mathbf{c}^* at $z = 1/2$.

For a reflection $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ of the first twin component, the corresponding reflection for the second twin component is located at $\mathbf{H}' = h\mathbf{a}'^* + k\mathbf{b}'^* + l\mathbf{c}^*$, where $\mathbf{a}'^* = \mathbf{a}^* - 2|a^*/c^*|(\cos \beta^*)\mathbf{c}^*$ and $\mathbf{b}'^* = \mathbf{b}^* - 2|b^*/c^*|(\cos \alpha^*)\mathbf{c}^*$. Note that $\mathbf{a}'^* \cdot \mathbf{c}'^* = \mathbf{a}^* \cdot \mathbf{c}^*$, $\mathbf{b}'^* \cdot \mathbf{c}'^* = \mathbf{b}^* \cdot \mathbf{c}^*$, and $\mathbf{c}'^* = -\mathbf{c}^*$. The nearest twin component for the first component is then $\mathbf{H}'' = h\mathbf{a}^* + k\mathbf{b}^* + l'\mathbf{c}^*$, where \mathbf{H}'' is the nearest reflection to $\mathbf{H}' = h\mathbf{a}'^* + k\mathbf{b}'^* - (l + 2h|a^*/c^*|(\cos \beta^*) + 2k|b^*/c^*|(\cos \alpha^*))\mathbf{c}^*$; i.e., l' is the integer nearest to $-(l - 0.3965h - 0.4993k)$ and the separation in reciprocal space is $(l' + l - 0.3965h - 0.4993k)\mathbf{c}^*$. When the mirror is repeated, the h, k, l' reflection of the second component is the reflection nearest to the h, k, l reflection of the first component with the same separation in reciprocal space. For convenience we will say l' is $-(l - 0.3965h - 0.5k)$, allowing values for the separation in reciprocal space of reflections from different twin components to be simply a function of h and whether k is odd or even. To a first approximation, assuming 0.3965 is exactly $2/5$, almost total overlap exists for $h = 5n$ when k is even, partial overlap exists for $h = 5n \pm 1$ when k is odd, and even less partial overlap exists for $h = 5n \pm 2$ when k is even; i.e., these are the instances when $|l' + l - 0.3965h - 0.5k| < 0.25$. We thus set $j = 0$ for the first twin component and $p_j = |h|$ for the second component, which only exists for the appropriate parity of k .

The procedure used works well and is assisted by the following. (i) When the overlapping reflection is much more intense than the reference reflection, the background error increases, increasing the standard error of the resulting intensity and thus reducing the weighting for such reflections in the refinement. Refinement only includes those reflections with $I > 3\sigma(I)$, and some of the most troublesome reflections get excluded from refinement. Reflections for which $I_{\text{calcd}} < 2.5\sigma(I)$ were also excluded from the refinement. (ii) It was found that excluding reflections with $(\sin \theta)/\lambda < 0.2$ was beneficial. The limited number of reflections in this range are better resolved than higher angle reflections. Their exclusion highlights this and allows the p_j values to decrease as a function of $|l' + l - 0.3965h - 0.5k|$ in a sensible fashion. The values for p_1 to p_{12} were found to be 0.775(15), 0.210(13), 0.298(14), 0.836(15), 0.947(15), 0.655(15), 0.152(19), 0.409(20), 0.822(25), 0.909(30), 0.469(47), and 0.066(85) with values for $|l' + l - 0.3965h - 0.5k|$ of 0.1035, 0.2070, 0.1895, 0.0860, 0.0175, 0.1210, 0.2245, 0.1720, 0.0685, 0.0350, 0.1385, and 0.2420.

The anisotropic refinement used a number of constraints. The three phenyl rings were constrained to have a common refinable planar geometry of $mm2$ symmetry relative to the P atom to which they are attached. All other non-hydrogen atom positional parameters were unconstrained. The atomic displacement parameters for the triphenylphosphine was modeled using TL rigid body models, with the T common to all atoms (6 parameters) and the librations (6 parameters per phenyl group) centered on the P atom. A 15-

parameter TLX model²⁷ was used for the group of atoms (C1–C3, C8–C11, O1). All other non-hydrogen atoms were refined as individual anisotropic atoms. Hydrogen atoms were reincluded after each refinement cycle in sensible calculated positions and given atomic displacement parameters determined by the atoms to which they are attached. The methyl hydrogens were included in two orientations of half-occupancy.

Concluding Remarks

The macrocyclization of TTDD by $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ is remarkable for the facility with which it proceeds under ambient conditions. This we attribute, in part, to the labilization of coligands by alkynes coordinated to 16-electron metal centers (2- vs 4-electron alkyne coordination).²⁰ However, the failure of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ to cyclize 2,8-decadiyne indicates that thioether coordination also plays a crucial role. While the synthesis of **2** is illustrative of a potential route to functionalized macrocyclic thioethers, the tenacity with which butadiene linkages bind to $d^8\text{-M}^0\text{L}_3$ fragments suggests that processes catalytic in metal will require extension of the principle to other metal centers.

Experimental Section

Synthesis of $[\text{Ru}(\text{CO})(\text{PPh}_3)(\{\eta^4\text{-S}(\text{C}_2\text{H}_4\text{SCCMe})_2\text{CO-}\kappa\text{-S}\})]$ (2**).** A mixture of $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_3]$ ¹¹ (2.00 g, 2.12 mmol) and 4,7,10-trithiatrideca-2,11-diyne (TTDD; 0.49 g, 2.12 mmol) was stirred in dry toluene under nitrogen at room temperature overnight. The pale yellow supernatant was decanted, and the yellow product was dried in vacuo. Yield: 1.00 g (75%). Mp: 226–228 °C. Anal. Calcd for $\text{C}_{30}\text{H}_{29}\text{O}_2\text{PRuS}_3$: C, 55.45; H, 4.50; P, 4.77; S, 14.80. Found: C, 55.72; H, 4.23; P, 4.80; S, 14.71. ¹H NMR (CD_2Cl_2 , 298 K, 300 MHz): δ 7.25 (m, 15 H, C_6H_5), 4.10 (ddd, 1 H, $J_{\text{HH}} = 13.7, 13.5, 2.5$ Hz, on C δ 28.6), 3.14 (ddd, 1 H, $J_{\text{HH}} = 14.8, 3.0, 3.0$ Hz, on C δ 40.3), 2.81 (ddd, 1 H, $J_{\text{HH}} = 15, 4.4, 2.8$ Hz, on C δ 28.6), 2.68 (ddd, 1 H, $J_{\text{HH}} = 13.3, 2.8, 2.7$ Hz, on C δ 27.3), 2.30 (ddd, 1 H, $J_{\text{HH}} = 14.8, 4.4, 2.4$ Hz, on C δ 20.7), 2.12 (ddd, 1 H, coupling not resolved, on C δ 40.3), 2.01 (d, 3 H, $J_{\text{HP}} = 1.4$ Hz, CH_3 on C δ 9.9, pseudo-trans to CO), 2.00 (ddd, 1 H, coupling not resolved, on C δ 27.3), 1.13 (ddd, 1 H, $J_{\text{HH}} = 14.9, 12.1, 2.9$ Hz, on C δ 20.7), 0.96 (d, 3 H, $J_{\text{HP}} = 4.1$ Hz, CH_3 on C δ 8.8, pseudo-trans to PPh_3). ¹³C{¹H} NMR (CD_2Cl_2 , 298 K, 75 MHz): δ 208.3 (br, RuCO), 155.0 (CCO), 134.6 (d, $^1J_{\text{CP}} = 45$, $\text{C}^1(\text{C}_6\text{H}_5)$), 133.9 (d, $J_{\text{CP}} = 12$, $\text{C}^{2,3,5,6}(\text{C}_6\text{H}_5)$), 130.5 (d, $^4J_{\text{CP}} = 2$, $\text{C}^4(\text{C}_6\text{H}_5)$), 128.7 (d, $J_{\text{CP}} = 10$ Hz, $\text{C}^{2,3,5,6}(\text{C}_6\text{H}_5)$), 97.8, 89.7, 80.8, 80.2 (C=C \times 4), 40.3 (CH_2 , α to C δ 27.3), 28.6 (CH_2 , α to C δ 20.7), 27.3 (CH_2 , α to C δ 40.3), 20.7 (CH_2 , α to C δ 28.6), 9.9 (CH_3 , pseudo-trans to CO), 8.8 (CH_3 , pseudo-trans to P). ³¹P{¹H} NMR (CD_2Cl_2 , 298 K, 121 MHz): δ 48.5 (s). IR (Nujol): 1918 (ν_{RuCO}), 1587, 1576, 1565 (ν_{CO}) cm^{-1} . IR (CH_2Cl_2): 1929 (ν_{RuCO}), 1561 (ν_{CO}) cm^{-1} . MS (FAB, positive ion, nba matrix): m/z 651 $[\text{M} + \text{H}]^+$, 623 $[\text{M} - \text{CO} + \text{H}]^+$ (isotopic distributions confirmed by simulation). Crystal data: $\text{C}_{30}\text{H}_{29}\text{O}_2\text{PRuS}_3$, $M_r = 649.78$, triclinic, $P\bar{1}$ (No. 2), $a = 9.4529(2)$ Å, $b = 11.2806(3)$ Å, $c = 13.1159(3)$ Å, $\alpha = 77.595(1)^\circ$, $\beta = 81.762(1)^\circ$, $\gamma = 89.895(1)^\circ$, $V = 1351.25(6)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.597$ g cm^{-3} , $T = 200$ K, yellow plate, 6144 independent measured reflections, $R1 = 0.052$, $wR2 = 0.063$, 4147 absorption-corrected reflections ($I > 3\sigma(I)$, $2\theta \leq 55^\circ$), 185 parameters.

Synthesis of $[\text{Ru}(\text{CO})(\text{dppe})(\{\eta^4\text{-S}(\text{C}_2\text{H}_4\text{SCCMe})_2\text{CO}\})]$ (6**).** A solution of **2** (0.13 g, 0.20 mmol) and dppe (0.076 g, 0.2 mmol) in toluene (30 mL) was heated under reflux for 2 h. The resulting pale yellow solution was cooled, filtered, and

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then freed of volatiles. The pale yellow product was washed with hexane and diethyl ether to remove PPh_3 and unreacted dppe. Yield: 0.092 g, 60%. Mp: 132–134 °C dec. $^1\text{H NMR}$ (298 K, 300 MHz, C_6D_6): δ 7.81, 7.30–7.0 (m \times 2, 20 H, C_6H_5), 2.7–2.3 (m, 8 H, SCH_2), 2.2–2.0 (m, 4 H, PCH_2), 1.62 (d, 6 H, $^3J_{\text{HP}} = 2$ Hz, CH_3). $^1\text{H NMR}$ (298 K, 300 MHz, CD_2Cl_2): δ 7.7–7.1 (m, 20 H, C_6H_5), 3.1–2.6 (m, 8 H, SCH_2), 2.6–2.4 (m, 4 H, PCH_2), 1.24 (s, 6 H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 75 MHz): δ 203.5 (br, RuCO), 171.6 (CO), 135.8 (d, $^1J_{\text{CP}} = 41$ Hz, $\text{C}^1(\text{C}_6\text{H}_5)$), 135.3 (d, $^1J_{\text{CP}} = 38$ Hz, $\text{C}^1(\text{C}_6\text{H}_5)$), 133.3 (d, $J_{\text{CP}} = 12$ Hz, $\text{C}^{2,3,5,6}(\text{C}_6\text{H}_5)$), 133.0 (d, $J_{\text{CP}} = 11$ Hz, $\text{C}^{2,3,5,6}(\text{C}_6\text{H}_5)$), 130.1 (s \times 2, $\text{C}^4(\text{C}_6\text{H}_5)$), remaining C_6H_5 resonances obscured by C_6D_6 , 95.3, 82.6 ($\text{C}=\text{C} \times 2$), 35.9, 32.6 (SCH_2), 30.0 (m, PCH_2), 9.2 (CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (298 K, 121 MHz, C_6D_6): δ 60.5 (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (298 K, 121 MHz, CD_2Cl_2): δ 63.0 (s).

IR (Nujol): 1936 (ν_{RuCO}), 1568 (ν_{CCO}) cm^{-1} . IR (CH_2Cl_2): 1933 (ν_{RuCO}), 1565 (ν_{CCO}) cm^{-1} . MS (APCI, positive ion, MeCN): m/z 824.8 [$\text{M} + \text{Na} + \text{O}$] $^+$, 786.8 [M] $^+$. Satisfactory elemental analytical data were not obtained, due to difficulties encountered in separating the product from dppe and PPh_3 (^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are provided in the Supporting Information).

Supporting Information Available: Tables giving crystallographic details for **2** and figures giving COSY (H–H) and HMQC (C–H correlation) spectra of **2** in CD_2Cl_2 and ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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