

One-Pot Synthesis of (η^6 -Arene)bis(triphenylphosphine)(methyl)ruthenium(II) Cations. X-ray Structures of [$(\eta^6$ -C₆H₆)Ru(Me)(PPh₃)₂]- [AlCl₂Me₂] and the η^5 -Thiophene Analogue

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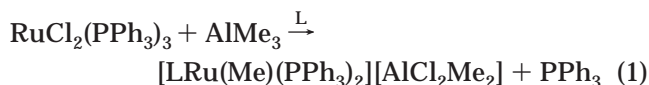
Summary: We report one-pot syntheses for a series of complexes of the type [$(\eta^6$ -arene)Ru^{II}Me(PPh₃)₂][AlCl₂Me₂] in high yields and X-ray structures of the η^6 -C₆H₆ and η^5 -thiophene derivatives. Other derivatives include fluorobenzene and mesitylene complexes, and all of the complexes are synthesized by addition of AlMe₃ to RuCl₂(PPh₃)₃ in the neat arene solvent or in an admixture with hexane for thiophene and fluorobenzene.

During our ongoing research on electrophilic cationic transition metal complexes, e.g., [Mn(CO)₃(P)₂(CH₂-Cl₂)⁺ and [RuCl(PP)₂]⁺ (P and PP = tied-back phosphite and diphosphonite),¹ we desired to prepare RuCl(Me)(PPh₃)₃. The intention was to remove the methyl group by well-established procedures¹ to possibly form 16e cationic solvato species such as [RuCl(PPh₃)₃(CH₂Cl₂)⁺ that could be useful precursors for small molecule binding or catalysts. The sought-after RuCl(Me)(PPh₃)₃ complex had been reported to be synthesized by a reaction of RuCl₂(PPh₃)₃ with AlMe₃ in benzene, but no NMR data were given.² By following the reported procedure, we isolated instead the complex [$(\eta^6$ -C₆H₆)Ru(Me)(PPh₃)₂][AlCl₂Me₂] (**1**) in high yield. η^6 -Arene-(alkyl)ruthenium(II) cations are related to various ruthenium-catalyzed organic transformations, most notably asymmetric synthesis, and therefore are of high significance.³ There is renewed interest in (arene)-ruthenium(II) complexes owing to the great stability of the metal–arene bond in these compounds compared to Cp analogues and their ability to act as effective precursors for catalytic asymmetric hydrogenation and to promote the synthesis of complex organic compounds.

For example heterobidentate P,O-donor ligands produce chiral metal centers when bound to arene-Ru complexes, and [(cymene)Ru(η^2 -chelate-P,O)Cl]⁺ cations are precursors to 16-electron dicationic strong Lewis acids that have potential use in asymmetric catalysis.^{3e}

The [(arene)Ru(Me)(PPh₃)₂]⁺ complexes we report here should be useful precursors for complexes of the above type and other arene-Ru species, e.g., by substitution of PPh₃ by chiral ligands. Yet, there is not a general synthesis reported for complexes of this type. A multistep synthesis of cation **1** with a PF₆⁻ counteranion was reported previously.⁴ We now have found a much easier one-pot synthesis for this arene methyl ruthenium(II) cation as well as heretofore unreported analogues with mesitylene (**2**), thiophene (**3**), and fluorobenzene (**4**) ligands. X-ray structures of complexes **1** and **3** show η^6 -coordination of benzene and η^5 -coordination of thiophene.

Complexes **1–4** are synthesized by reaction of commercially available RuCl₂(PPh₃)₃ with a 2- to 4-fold excess of AlMe₃ in the presence of benzene, mesitylene, thiophene, and fluorobenzene, respectively (Scheme 1). In the case of **3** and **4**, hexane solvent is used to reduce the amount of arene reagents, and the reaction mixtures are stirred for 2–3 days because of the poor solubility of RuCl₂(PPh₃)₃ in this solvent. These complexes are presumably formed in a multistep mechanism involving replacement of chloride ligands by methyl and by displacement of PPh₃ from Ru by an arene or thiophene molecule L (eq 1).



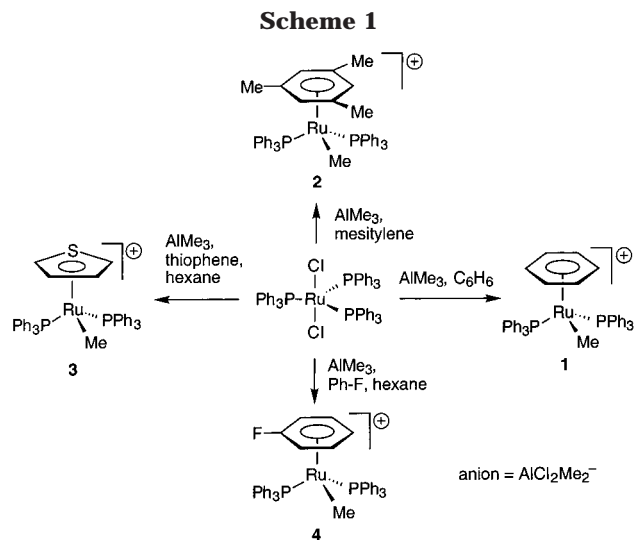
The elimination of PPh₃ is perhaps aided by association of AlMe₃ or a similarly Lewis-acidic derivative such as AlClMe₂ to the phosphine. The arene and thiophene complexes are isolated as yellow solids in good yields (e.g., 85% for **1**). NMR spectroscopy and crystallography show primarily the presence of AlCl₂Me₂⁻ counteranions and not mixed anions such as AlClMe₃⁻ in the isolated products. However satisfactory elemental analyses were difficult to obtain in some cases, particularly for **4**,

(1) (a) Fang, X.-G.; Vincent, J. H.; Scott, B. L.; Kubas, G. J. *J. Organomet. Chem.* **2000**, *609*, 95. (b) Fang, X.-G.; Scott, B. L.; John, K. D.; Kubas, G. J. *Organometallics* **2000**, *19*, 4141. (c) Fang, X.; Scott, B. L.; Watkin, J. G.; Kubas, G. J. *Organometallics* **2001**, *20*, 2413. (d) Huhmann-Vincent, J.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **1998**, *120*, 6808. (e) Huhmann-Vincent, J.; Scott, B. L.; Kubas, G. J. *Inorg. Chem.* **1999**, *38*, 115. (f) Huhmann-Vincent, J.; Scott, B. L.; Kubas, G. J. *Inorg. Chim. Acta* **1999**, *294*, 240.

(2) Porter, R. A.; Shriver, D. F. *J. Organomet. Chem.* **1975**, *90*, 41.

(3) For selected recent examples, see: (a) Ceccanti, A.; Diversi, P.; Ingrosso, G.; Laschi, F.; Lucherini, A.; Magagna, S.; Zanella, P. *J. Organomet. Chem.* **1996**, *526*, 251. (b) LeGendre, P.; Offenbecher, M.; Bruneau, C.; Dixneuf, P. H. *Tetrahedron: Asymmetry* **1998**, *9*, 2279. (c) Faller, J. W.; Patel, B. P.; Albrizio, M. A.; Curtis, M. *Organometallics* **1999**, *18*, 3096. (d) Furstner, A.; Liebl, M.; Lehmann, C. W.; Picquet, M.; Kunz, R.; Bruneau, C.; Touchard, D.; Dixneuf, P. H. *Chem. Eur. J.* **2000**, *6*, 1847. (e) Faller, J. W.; Liu, X.; Parr, J. *Chirality* **2000**, *12*, 325. (f) Arena, C. G.; Calamia, S.; Faraone, F.; Graiff, C.; Tiripicchio, A. *Dalton* **2000**, 3149. For a review, see: Lebozec, H.; Touchard, D.; Dixneuf, P. H. *Adv. Organomet. Chem.* **1989**, *29*, 163.

(4) Werner, R.; Werner, H. *Chem. Ber.* **1982**, *115*, 3781.



indicating the anion composition could be mixed to a minor degree or the anion is sensitive to degradation by trace air or moisture. The $\text{AlCl}_2\text{Me}_2^-$ anion has previously been reported to form in a reaction of a 4-fold excess of AlMe_3 with YbCl_3 in toluene in a sealed tube (12 h, 80 °C) to form $[\text{YbCl}_2(15\text{-crown-5})][\text{AlCl}_2\text{Me}_2]$ in the presence of 15-crown-5.⁵ The anion was stated to impart air-sensitivity to the complex, and its composition was revealed in the X-ray structure of the Yb complex. The authors surmised that anions ranging from AlMe_4 to AlCl_4 were probably present in solution and that $[\text{AlCl}_2\text{Me}_2]^-$ formed the least soluble species when paired with the cation. The aluminate anion in **1** can readily be replaced by borate-type anions as discussed below. As shown in Scheme 1, the synthesis of the arene cations works for both electron-rich (mesitylene) and electron-poor ($\text{C}_6\text{H}_5\text{F}$) arenes as well as aromatic heterocycles (thiophene). However, when for example hexane or C_6F_6 is used as the sole solvent, a clean product could not be isolated in our hands.

The ^1H NMR spectra of **1–4** in CDCl_3 all show a sharp singlet for the methyl groups in the $\text{AlCl}_2\text{Me}_2^-$ anion near $\delta -0.6$ and a triplet for the Ru-bound Me at $\delta 1.11\text{--}1.34$ ($J_{\text{PH}} = 5.5\text{--}6.2$ Hz), generally with the appropriate 2:1 signal integration. The Me signal for the fluorobenzene complex is actually a doublet of triplets with an additional small coupling of 2.4 Hz. This is presumably due to coupling of the Ru-Me hydrogens to fluorine. The ^1H signal for the $\eta^6\text{-C}_6\text{H}_6$ ligand in **1** is a singlet at $\delta 5.51$. ^{13}C NMR chemical shifts of the coordinated arenes and thiophene in **1–4** all shift upfield in comparison to those of the free arenes and thiophene, which is typical for such ligands bound to transition metals. For instance, coordinated thiophene has ^1H and ^{13}C chemical shifts of $\delta 5.32$ (CH), 5.86 (CH), 94.3 (CH), and 95.0 (CH), while the chemical shifts of free thiophene are $\delta 7.31$, 7.50, 123.8, and 125.5, respectively. The ^{31}P NMR chemical shifts range from $\delta 42.0$ to 48.5. The $\text{AlCl}_2\text{Me}_2^-$ counteranion in **1** can be replaced by BAR_F^- ($[\text{B}(3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3)_4]^-$) by reacting $[\text{Ph}_3\text{C}][\text{BAR}_\text{F}]$ ⁶ with **1** in CH_2Cl_2 . The trityl cation apparently removes a methyl group from the anion to

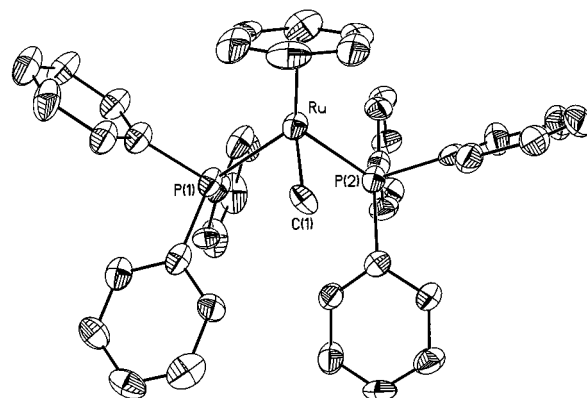


Figure 1. Thermal ellipsoid plot (50% probability ellipsoids) of $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{Me})(\text{PPh}_3)_2][\text{AlMe}_2\text{Cl}_2]\cdot\text{CH}_2\text{Cl}_2$, **1**· CH_2Cl_2 .

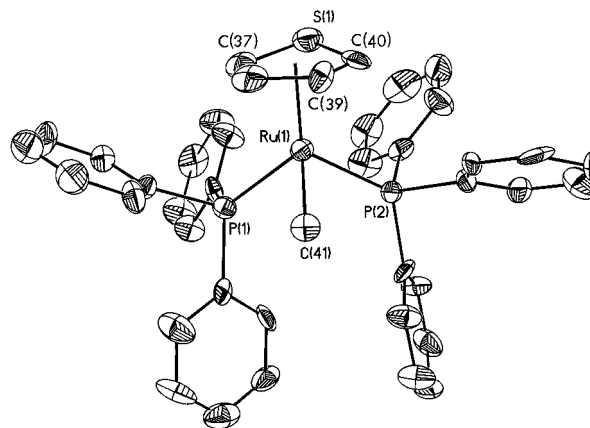


Figure 2. Thermal ellipsoid plot (50% probability ellipsoids) of $[(\eta^5\text{-thiophene})\text{Ru}(\text{Me})(\text{PPh}_3)_2][\text{AlMe}_2\text{Cl}_2]\cdot\text{CH}_2\text{Cl}_2$, **3**· CH_2Cl_2 .

form Ph_3CMe and AlCl_2Me rather than removing Me from the metal, which would have been desirable to form highly electrophilic dicationic species such as $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)_2(\text{S})]^{2+}$ ($\text{S} = \text{solvent}$). Indeed, no reactions of $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{Me})(\text{PPh}_3)_2][\text{BAR}_\text{F}]$ with either $[\text{Ph}_3\text{C}][\text{BAR}_\text{F}]$ or $[\text{H}(\text{OEt}_2)_2][\text{BAR}_\text{F}]$ were found to occur. Treatment with HOSO_2CF_3 apparently does remove the methyl group as methane, but a clean product was not obtained.

The η^6 -coordination of arene and η^5 -coordination of thiophene and the presence of $\text{AlCl}_2\text{Me}_2^-$ anions are confirmed by single-crystal X-ray analysis for compounds **1**· CH_2Cl_2 and **3**· CH_2Cl_2 (Figures 1 and 2; Tables 1 and 2). There are many structural studies of arene coordination, and the X-ray structure of the cation of **1** is unexceptional. Although there are far fewer η^5 -thiophene complexes, the structural features of the thiophene ligand in **3** generally are similar to those observed in other transition metal complexes containing similarly bound thiophene and thiophene derivatives.⁷ Although it is not a significant feature of the structures, the nature of the anion in **1** and **3** is somewhat more problematic. From the X-ray data the molecular formula calculates as $\text{AlCl}_2\text{Me}_2^-$, which agrees with NMR integration of methyl groups and elemental analyses for the most part, but may be a nominal composition where a

(5) Atwood, D. A.; Bott, S. G.; Atwood, J. L. *J. Coord. Chem.* **1987**, 17, 93.

(6) Bahr, S. R.; Boudjouk, P. *J. Org. Chem.* **1992**, 57, 5545.

(7) (a) Polam, J. R.; Porter, L. C. *Organometallics* **1993**, 12, 3504, and references therein. (b) Angelici, R. J. *NATO ASI Ser., Ser. 3* **1998**, 60 (*Transition Metal Sulphides*), 89.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{Me})(\text{PPh}_3)_2]\text{-}[\text{AlMe}_2\text{Cl}_2]\cdot\text{CH}_2\text{Cl}_2, 1\cdot\text{CH}_2\text{Cl}_2$

Ru–C(1)	2.124(9)
Ru–C _{benzene}	2.276(10)–2.334(13)
Ru–centroid _{benzene}	1.813
Ru–P(2)	2.368(3)
Ru–P(1)	2.402(3)
C–C (benzene)	1.391(18)–1.426(17)
Al–C (anion)	2.004(9), 2.041(9)
Al–Cl (anion)	2.198(5), 2.238(5)
C(1)–Ru–P(2)	86.3(3)
C(1)–Ru–P(1)	89.8(3)
P(2)–Ru–P(1)	97.39(9)
C–Al–C (anion)	109.2(5)
Cl–Al–Cl (anion)	102.8(2)
C–Al–Cl (anion)	107.3(3)–112.0(4)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[(\eta^5\text{-Thiophene})\text{Ru}(\text{Me})(\text{PPh}_3)_2]\text{-}[\text{AlMe}_2\text{Cl}_2]\cdot\text{CH}_2\text{Cl}_2, 3\cdot\text{CH}_2\text{Cl}_2$

Ru(1)–C(41)	2.168(7)
Ru(1)–S(1)	2.515(2)
Ru(1)–C(37)	2.208(9)
Ru(1)–C(38)	2.245(8)
Ru(1)–C(39)	2.212(8)
Ru(1)–C(40)	2.241(7)
Ru(1)–centroid _{thiophene}	1.881
Ru(1)–P(2)	2.335(2)
Ru(1)–P(1)	2.346(2)
S(1)–C(37)	1.728(10)
S(1)–C(40)	1.756(9)
C(37)–C(38)	1.420(11)
C(38)–C(39)	1.450(12)
C(39)–C(40)	1.388(11)
C(41)–Ru(1)–P(2)	87.0(2)
C(41)–Ru(1)–P(1)	86.5(2)
P(2)–Ru(1)–P(1)	103.05(8)

mix of AlCl_3Me^- and AlClMe_3^- anions could be present to a minor degree. Temperature factors show some disorder of the anion in the benzene structure and to a greater extent in the thiophene structure, where it is extensive enough that it could be modeled. Unfortunately, it is not possible to know if the disorder is positional (orientational difference of the $\text{AlCl}_2\text{Me}_2^-$ from cell to cell) or substitutional (mixture of AlCl_3Me^- and AlClMe_3^-). Most likely the dominant anion is $\text{AlCl}_2\text{Me}_2^-$, however, as in the previously mentioned structure of $[\text{YbCl}_2(15\text{-crown-5})][\text{AlCl}_2\text{Me}_2]$ (the anion was not reported to be disordered here).⁵

In summary, a general one-pot synthesis of (arene)-(PPh₃)₂(Me)Ru(II) cations has been developed, including a η^5 -thiophene analogue. The $\text{AlCl}_2\text{Me}_2^-$ counteranion in **1** can be replaced by BAR_F^- by reaction with $[\text{Ph}_3\text{C}][\text{BAR}_F]$, which removes a methyl group from the anion rather than from the metal. X-ray analysis confirms the η^6 -coordination of arene and η^5 -coordination of thiophene.

Experimental Section

All manipulations were performed either under a helium atmosphere in a Vacuum Atmospheres drybox or under an argon atmosphere using standard Schlenk techniques unless otherwise specified. CH_2Cl_2 was distilled under Ar from P_2O_5 . Hexane was purified by passing through columns of activated alumina and activated Cu-0226 S copper catalyst (Engelhard). Benzene, mesitylene, and fluorobenzene were purchased from Aldrich and dried under 4 Å molecular sieves. Other reagents were purchased from Aldrich, Acros, Fluka, or Strem Chemical Co. and used as received. ¹H, ³¹P, and ¹³C spectra were

recorded on a Varian Unity 300 spectrometer with field strengths of 300, 121, and 75 MHz, respectively. ¹H and ¹³C chemical shifts were referenced to the residual solvent resonance relative to TMS; ³¹P chemical shifts were referenced to external 85% H_3PO_4 . Elemental analyses were performed in house on a Perkin-Elmer Series II CHNS/O model 2400 analyzer.

$[(\eta^6\text{-Benzene})\text{bis}(\text{triphenylphosphine})(\text{methyl})\text{ruthenium}][\text{AlCl}_2\text{Me}_2]$ (1**).** AlMe_3 (2 M in hexane, 0.16 mL, 0.31 mmol) was added to a suspension of $\text{RuCl}_2(\text{PPh}_3)_3$ (0.200 g, 0.208 mmol) in benzene (9 mL), and the resulting mixture was stirred for 3 h at RT to give a yellow suspension. The suspension was filtered, and the solid was washed with hexane (3×) to give the product (0.150 g, 85%) as yellow solids. ¹H NMR (CDCl_3): δ –0.57 (s, 6H), 1.24 (t, 3H, $J_{\text{PH}} = 6.2$ Hz), 5.51 (s, 6H), 7.07–7.42 (m, 30H). ³¹P NMR (CDCl_3): δ 42.5. ¹³C NMR (CD_2Cl_2): δ –17.2 (t, $J = 15.0$ Hz), 97.4, 128.8 (t, $J = 4.5$ Hz), 131.0, 134.0 (t, $J = 4.3$ Hz), 134.8 (t, $J = 22.7$ Hz). ¹H NMR and elemental analysis indicated the presence of lattice benzene. Anal. Calcd for $\text{C}_{45}\text{H}_{45}\text{AlCl}_2\text{P}_2\text{Ru}\cdot 0.2\text{C}_6\text{H}_6$: C, 65.95; H, 5.50. Found: C, 65.77; H, 5.74.

$[(\eta^6\text{-Benzene})\text{bis}(\text{triphenylphosphine})(\text{methyl})\text{ruthenium}][\text{BAR}_F]$. A solution of **1** (66 mg, 0.078 mmol) in CH_2Cl_2 (2 mL) was treated with $[\text{Ph}_3\text{C}][\text{BAR}_F]$ (90 mg, 0.081 mmol) for 30 min. Volatiles were removed and the residue was washed with hexane. ³¹P and ¹H NMR spectra were similar to that for **1** but showed the absence of the aluminate anion Me signals. Anal. Calcd for $\text{C}_{75}\text{H}_{51}\text{F}_{24}\text{P}_2\text{BRu}$: C, 56.92; H, 3.22. Found: C, 56.43; H, 3.85.

$[(\eta^6\text{-Mesitylene})\text{bis}(\text{triphenylphosphine})(\text{methyl})\text{ruthenium}][\text{AlCl}_2\text{Me}_2]$ (2**).** AlMe_3 (2 M in hexane, 0.16 mL, 0.31 mmol) was added to a suspension of $\text{RuCl}_2(\text{PPh}_3)_3$ (0.158 g, 0.16 mmol) in mesitylene (2 mL), and the resulting mixture was stirred for 3 h at RT to give a yellow suspension. The suspension was filtered and the solid was washed with hexane (3×) to give the product as yellow solids that contain mesitylene. Crystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$ at –30 °C afforded the product (0.095 g, 67%) as yellow crystals containing a lattice CH_2Cl_2 as indicated by ¹H NMR and elemental analysis. ¹H NMR (CDCl_3): δ –0.58 (s, 6H), 1.11 (t, 3H, $J_{\text{PH}} = 6.0$ Hz), 1.75 (s, 9H), 5.22 (s, 3H), 5.33 (2H, CH_2Cl_2), 7.02–7.41 (m, 30H). ³¹P NMR (CDCl_3): δ 48.2. ¹³C NMR (CD_2Cl_2): δ –8.9 (t, $J = 4.9$ Hz), 19.1, 95.8, 115.7, 128.4, 131.0, 133.5 (t, $J = 22.0$ Hz), 134.8. Anal. Calcd for $\text{C}_{48}\text{H}_{51}\text{AlCl}_2\text{P}_2\text{Ru}\cdot\text{CH}_2\text{Cl}_2$: C, 60.43; H, 5.45. Found: C, 60.34; H, 5.56.

$[(\eta^5\text{-Thiophene})\text{bis}(\text{triphenylphosphine})(\text{methyl})\text{ruthenium}][\text{AlCl}_2\text{Me}_2]$ (3**).** AlMe_3 (2 M in hexane, 0.15 mL, 0.30 mmol) was added to a suspension of $\text{RuCl}_2(\text{PPh}_3)_3$ (0.100 g, 0.10 mmol) in hexane (3 mL) and thiophene (0.2 mL), and the resulting mixture was stirred for 3 days at RT to give a yellow suspension. The suspension was filtered and the solid was washed with hexane (3×) to give the product (0.061 g, 72%) as yellow solids. ¹H NMR (CDCl_3): δ –0.62 (s, 6H), 1.18 (t, 3H, $J_{\text{PH}} = 5.8$ Hz), 5.36 (br, 2H), 5.86 (br, 2H), 7.03–7.44 (m, 30H). ³¹P NMR (CDCl_3): δ 46.9. ¹³C NMR (CDCl_3): δ –11.5 (br), 94.3, 95.0, 128.9, 130.8, 133.6, 134.1 (t, $J = 22.5$ Hz). Anal. Calcd for $\text{C}_{43}\text{H}_{43}\text{AlCl}_2\text{P}_2\text{SRu}$: C, 60.56; H, 5.04. Found: C, 59.72; H, 5.51.

$[(\eta^6\text{-Fluorobenzene})\text{bis}(\text{triphenylphosphine})(\text{methyl})\text{ruthenium}][\text{AlCl}_2\text{Me}_2]$ (4**).** AlMe_3 (2 M in hexane, 0.20 mL, 0.40 mmol) was added to a suspension of $\text{RuCl}_2(\text{PPh}_3)_3$ (0.100 g, 0.10 mmol) in hexane (3 mL) and fluorobenzene (0.2 mL), and the resulting mixture was stirred for 2 days at RT to give a yellow suspension. The suspension was filtered and the solid was washed with hexane (3×) to give a yellow solid. The solid was crystallized from $\text{CH}_2\text{Cl}_2/\text{hexane}$ to afford the product (0.060 g, 71%) as yellow solids. ¹H NMR (CDCl_3): δ –0.56 (s, 6H), 1.34 (dt, 3H, $J_{\text{PH}} = 5.5$ Hz; $J_{\text{FH}} = 2.4$ Hz), 4.43 (t, 2H, $J = 5.5$ Hz), 5.50 (br, 2H), 6.50 (br, 1H), 7.05–7.45 (m, 30H). ³¹P NMR (CDCl_3): δ 42.0. ¹³C NMR (CDCl_3): δ –5.1 (br), 78.4 (d, $J = 19.2$ Hz), 93.8, 100.6, 128.8, 131.2, 133.8. Although a

Table 3. Crystal Data and Structure Refinement for $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{Me})(\text{PPh}_3)_2][\text{AlMe}_2\text{Cl}_2]\cdot\text{CH}_2\text{Cl}_2, \mathbf{1}\cdot\text{CH}_2\text{Cl}_2$

empirical formula	$\text{C}_{46}\text{H}_{47}\text{AlCl}_4\text{P}_2\text{Ru}$
fw	931.63
temperature	203(2) K
wavelength	0.71073 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 11.856(2)$ Å, $\alpha = 89.52(3)^\circ$ $b = 13.529(3)$ Å, $\beta = 84.92(3)^\circ$ $c = 15.098(3)$ Å, $\gamma = 68.94(3)^\circ$
volume	2250.3(8) Å ³
Z	2
density (calcd)	1.375 Mg/m ³
abs coeff	0.707 mm ⁻¹
$F(000)$	956
cryst size	0.19 × 0.11 × 0.05 mm ³
θ range for data collection	1.61–22.46°
index ranges	–12 ≤ h ≤ 12, –14 ≤ k ≤ 14, –15 ≤ l ≤ 16
no. of reflns collected	5846
no. of ind reflns	4773 [$R(\text{int}) = 0.0714$]
max. and min. transmn	0.9655 and 0.8773
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	4773/0/487
goodness-of-fit on F^2	1.072
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0660$, $wR2 = 0.1578$
R indices (all data)	$R1 = 0.1037$, $wR2 = 0.2024$
largest diff peak and hole	0.886 and –1.850 e Å ⁻³

satisfactory carbon analysis was not obtained possibly because of the sensitive nature and/or mixed composition of the anion, the NMR data are clean and analogous to that for **1–3**.

X-ray Crystallographic Analyses. Crystals of **1**·CH₂Cl₂ were grown from CH₂Cl₂/hexane and mounted onto a glass fiber using a spot of silicone grease. Due to air-sensitivity, the crystal chosen was mounted from a pool of mineral oil under argon gas flow. The crystal was placed on a Bruker P4/CCD diffractometer, and cooled to 203 K using a Bruker LT-2 temperature device. The instrument was equipped with a sealed, graphite-monochromatized Mo K α X-ray source ($\lambda = 0.71073$ Å). A hemisphere of data was collected using φ scans, with 30 s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement were handled using SMART⁸ software. Frame integration, including Lorentz–polarization corrections, and final cell parameter calculations were carried out using SAINT⁹ software. The data were corrected for absorption using the SADABS¹⁰ program. Decay of reflection intensity was monitored via analysis of redundant frames. The structure was solved using direct methods and difference Fourier techniques. All hydrogen atom positions were idealized and rode on the atom they were attached to. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL NT.¹¹ Additional details of data collection and structure refinement are listed in Table 3.

Crystals of **3**·CH₂Cl₂ were grown from CH₂Cl₂/hexane, and a yellow-orange, irregularly shaped crystal was mounted onto a glass fiber using a spot of silicone grease. The data collection and structure solution were as above. Four independent

(8) SMART-NT 4; Bruker AXS, Inc.: Madison, WI 53719, 1996.

(9) SAINT-NT 5.050; Bruker AXS, Inc.: Madison, WI 53719, 1998.

(10) Sheldrick, G. SADABS, first release; University of Göttingen: Germany.

(11) SHELXTL NT, Version 5.10; Bruker AXS, Inc.: Madison, WI 53719, 1997.

Table 4. Crystal Data and Structure Refinement for $[(\eta^5\text{-Thiophene})\text{Ru}(\text{Me})(\text{PPh}_3)_2][\text{AlMe}_2\text{Cl}_2]\cdot\text{CH}_2\text{Cl}_2, \mathbf{3}\cdot\text{CH}_2\text{Cl}_2$

empirical formula	$\text{C}_{44}\text{H}_{45}\text{AlCl}_4\text{P}_2\text{RuS}$
fw	937.65
temperature	203(2) K
wavelength	0.71073 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 18.1777(11)$ Å, $\alpha = 80.688(2)^\circ$ $b = 19.8036(9)$ Å, $\beta = 80.032(1)^\circ$ $c = 25.2070(13)$ Å, $\gamma = 78.652(1)^\circ$
volume	8685.4(8) Å ³
Z	8
density (calcd)	1.434 Mg/m ³
abs coeff	0.780 mm ⁻¹
$F(000)$	3840
cryst size	0.29 × 0.21 × 0.12 mm ³
θ range for data collection	1.06–25.35°
index ranges	–21 ≤ h ≤ 21, –23 ≤ k ≤ 23, 0 ≤ l ≤ 30
no. of reflns collected	33 002
no. of ind reflns	27825 [$R(\text{int}) = 0.0238$]
max. and min. transmn	0.9122 and 0.8054
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	27825/6/1499
goodness-of-fit on F^2	1.027
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0820$, $wR2 = 0.1945$
R indices (all data)	$R1 = 0.1506$, $wR2 = 0.2246$
largest diff peak and hole	1.285 and –0.721 e Å ⁻³

molecules were present in the unit cell, and the Supporting Information presents data for all four (the C–C distances in the phenyl rings of PPh₃ were constrained to 1.3900 Å and the C–C–C angles to 120°). Anomalous temperature factors on the AlMe₂Cl₂ anions suggested disorder; the methyl carbon atoms had very small anisotropic displacement parameters, and the chloride atoms had moderately large anisotropic displacement parameters. The carbon atom positions with small ADPs were modeled as partial occupancy chlorine atoms, with variable site occupancy factors tied to one. All hydrogen atom positions in the (thiophene)Ru(Me)(PPh₃)₂ cation were idealized and rode on the atom they were attached to. Hydrogen atom positions of the disordered anions were not included in the final model. Eight disordered dichloromethane molecules were squeezed out of the unit cell ($Z = 8$) using PLATON/SQUEEZE.¹² The final refinement included anisotropic temperature factors on all non-hydrogen atoms, except for the anion chloride and carbon atoms. The anisotropic temperature factors of C(79), a thiophene carbon not bonded to S, were restrained to approximate isotropic behavior to prevent them from going nonpositive definite. Structure solution, refinement, graphics, and creation of publication materials were as above. Additional details of data collection and structure refinement are listed in Table 4.

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Supporting Information Available: X-ray crystallographic data of the structures of compounds **1**·CH₂Cl₂ and **3**·CH₂Cl₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) PLATON: Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.