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Organometallic Macrocycle Chemistry. 5.[1] σ-Vinyl and σ-Aryl Complexes of Ruthenium(II) Ligated by 1,4,7-Trithiacyclononane: X-ray Crystal Structure of $[Ru(CH{=}CH_2)(CO)(PPh_3)([9]aneS_3)]PF_6\cdot 2CH_2Cl_2$

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The reaction of coordinatively unsaturated σ-vinyl complexes $[Ru(CR{=}CHR')Cl(CO)(PPh_3)_2]$ with 1,4,7-trithiacyclononane ($[9]aneS_3$) provides chiral salts of the “half-sandwich” complexes $[Ru(CR{=}CHR')(CO)(PPh_3)([9]aneS_3)]^+$. The synthesis of the σ-aryl complex $[Ru(C_6H_4Me\text{-}4)(CO)(PPh_3)([9]aneS_3)]^+$ is also described. A representative NMR study of one example allowed the assignment of individual chemical shifts for the 12 diastereotopic proton environments of the macrocycle. The crystal structure of $[Ru(CH{=}CH_2)(CO)(PPh_3)([9]aneS_3)]PF_6\cdot 2CH_2Cl_2$ is also reported.

Introduction

The coordination chemistry of crown thioethers has previously been preoccupied with simple 1:1 or 2:1 adducts with metal halides or oxo halides.[2] Scattered reports have dealt with organometallic complexes ligated by the facially coordinating tridentate thioether 1,4,7-trithiacyclononane ($[9]aneS_3$); however, these have involved typically “innocent” ligands, e.g., CO,[3] benzene,[4] cyclopentadienyl,[5] and recently olefins.[6] The series of rhodium(I) complexes described by Schröder[6] are of interest in that they are reported to oxidatively add dihalomethanes to provide σ-halomethyl derivatives, these being rare examples of σ-alkyl complexes ligated by thioether macrocycles. We have been prompted to investigate the organometallic chemistry of sulfur-based macrocycles[7] by a suggestion[2a] that these ligands might emulate the properties associated with phosphine ligands, while offering the advantage of coordination sphere robustness typical of macrocycle complexes. Thus, while phosphines characteristically break down under more extreme conditions of industrial catalysis *via* P−C bond cleavage reactions, it was suggested that this problem would not arise with crown thioethers. We report herein the synthesis of a range of σ-vinyl and σ-aryl complexes ligated by 1,4,7-trithiacyclononane as representatives of species that might serve as model compounds in the subsequent development of alkene-modification and C_1 coupling catalysts. Aspects of the work have been communicated in preliminary form.[8]

Experimental Section

General Procedures. All manipulations were carried out under aerobic conditions. Solvents, alkynes, and the ligand $[9]aneS_3$ were used as received from commercial sources. ^1H, ^{13}C, and $^{31}P-\{^1H\}$ NMR spectra were recorded on a Bruker WH-400 or JEOL GX-270 NMR spectrometer and referenced against internal Me_4Si (^1H), $CDCl_3$ (^{13}C) or external H_3PO_4 (^{31}P). For the purposes of NMR assignments the vinyl substituents are designated according to Figure 1. In some instances, the poor solubility of the $[RuR(CO)(PPh_3)([9]aneS_3)]^+$ (**2**$^+$) salts precluded the convenient obtention of ^{13}C NMR data; however, representative examples [$R = CH{=}CH_2$, C_6H_4Me, and $C(C{\equiv}CPh){=}CHPh$] are included. Infrared spectra were recorded using a Perkin-Elmer 1720-X FT-IR spectrometer. Characteristic infrared absorbances for PPh_3 are

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(1) Part 4: Hector, A. L.; Hill, A. F. *Inorg. Chem.* **1995**, *34*, 3797.

(2) Cooper, S.; Rawle, S. C. *Struct. Bond.* **1990**, *72,* 1. Blake, A. J.; Schröder, M. *Adv. Inorg. Chem.* **1990**, *35*, 1.

(3) Adams, R. D.; Yamamoto, J. H. *Organometallics* **1995**, *14*, 3704. Adams, R. D.; Falloon, S. B.; McBride, K. T.; Yamamoto, J. H. *Organometallics* **1995**, *14*, 1739. Smith R. J.; Salek, S. N.; Went, M. J.; Blower, P. J.; Barnard, N. J. *J. Chem. Soc., Dalton Trans.* **1994**, 3165. Mohmand, G. F.; Thiele, K.; Went, M. J. *J. Organomet. Chem.* **1994**, *471*,.241. Laurenczy, G.; Merbach, A. E.; Moullet, B.; Roulet, R.; Hoferkamp, L.; Suss-Fink, G. *Helv. Chim. Acta* **1993**, *76*, 2936. Blake, A. J.; Halcrow, M. A.; Schröder, M. *Acta Crystallogr., Sect. C* **1993**, *49*, 85. Rossi, S.; Kallinen, K.; Pursiainen, J.; Pakkanen, T. T.; Pakkanen, T. A., *J. Organomet. Chem.* **1992**, *440*, 367. Hoferkamp, L.; Rheinwald, G.; Stoeklievans, H.; Suss-Fink, G. *Helv. Chim. Acta* **1992**, *75*, 2227. Castro, H. H. K.; Hissink, C. E.; Teuben, J. H.; Vaalburg, W.; Panek, K. *Rec. Trav. Chim. Pays-Bas* **1992**, *111*, 105. Haefner, S. C.; Dunbar, K. R.; Bender, C. *J. Am. Chem. Soc.* **1991**, *113*, 9540. Kim, H. J.; Do, Y. K.; Lee, H. W. Jeong, J. H.; Sohn, Y. S. *Bull. Kor. Chem. Soc.* **1991**, *12*, 257. Smith, R. J.; Admans, G. D.; Richardson, A. P.; Kuppers, H. J.; Blower, P. J. *J. Chem. Soc., Chem. Commun.* **1991**, 475. Sellmann, D.; Neuner, H. P.; Moll, M.; Knoch, F. *Z. Naturforsch.* **1991**, *46b*, 303. Elias, H.; Schmidt, G.; Kuppers, H. J.; Saher, M.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1989**, *28*, 3021. Pomp, C.; Brueke, S.; Kuppers, H. J.; Wieghardt, K.; Kruger, C.; Nuber, B.; Weiss, J. *Z. Naturforsch.* **1988**, *43b*, 299. Ashby, M. T.; Lichtenberger, D. L. *Inorg. Chem.* **1985**, *24*, 636. Sellmann, D.; Zapf, L. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 807.

(4) Bell, M. N.; Blake, A. J.; Christie, R. M.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Schröder, M.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1992**, 2977. Bennett, M. A.; Goh, L. Y.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1180.

(5) Blake, A. J.; Crofts, R. D.; Reid, G.; Schröder, M. *J. Organomet. Chem.* **1989**, *359*, 371.

(6) Blake, A. J.; Halcrow, M. A.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1994**, 1631. Blake, A. J.; Gould, R. O.; Halcrow, M. A.; Schröder, M. *Ibid*. **1994**, 2197.

(7) Alcock, N. W.; Cannadine, J. C.; Clark, G. R.; Hill, A. F. *J. Chem. Soc., Dalton Trans.* **1993**, 1131. Hill, A. F.; Alcock, N. W.; Cannadine, J. C.; Clark, G. R. *J. Organomet. Chem.* **1992**, *426*, C40.

(8) Cannadine, J.; Hector, A. L.; Hill, A. F. *Organometallics* **1992**, *11*, 2323.

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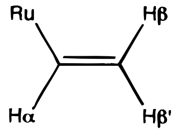

Figure 1. Vinyl substituent designation.

not listed. FAB mass spectrometry was carried out using an Autospec-Q mass spectrometer employing nitrobenzyl alcohol as matrix. Assignments are based on "M" representing the complex cation of the salts. Synthetic procedures for the complexes [Ru(CR=CHR′)Cl(CO)(PPh$_3$)$_2$],[9,10] [Ru(C$_6$H$_4$Me-4)Cl(CO)(PPh$_3$)$_2$],[11] [RuHCl(CO)(PPh$_3$)$_3$],[12] [RuH(NCMe)$_2$(CO)(PPh$_3$)$_2$]BF$_4$,[13] and [Ru{C(C≡CPh)=CHPh}Cl(CO)(PPh$_3$)$_2$][14] have been described elsewhere.

Synthesis of [Ru(CH=CH$_2$)Cl(CO)(PPh$_3$)$_2$] (1a). [RuHCl(CO)(PPh$_3$)$_3$] (0.40 g, 0.42 mmol) was suspended in dichloromethane (50 mL) and a stream of acetylene passed through the suspension for 30 s resulting in a deep orange solution. The color darkened over a period of 15 min of stirring. Ethanol (20 mL) was added, and the mixture concentrated under reduced pressure to provide orange crystals. These were isolated by filtration, washed with ethanol (10 mL) and petroleum ether (10 mL), and dried. Yield: 0.30 g (quantitative). IR (Nujol): 1918vs [ν(CO)], 1566m [ν(C=C)], 1215m, 851w cm^{-1}; (CH$_2$Cl$_2$) 1933vs [ν(CO)], 1559w [ν(C=C)] cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H δ 4.51 [dd, 1 H, Hβ, J(H$\alpha\beta$) = 13.9 Hz, J(H$\beta\beta'$) = 2.0 Hz], 5.11 [m, 1 H, Hβ'], 7.41, 7.60 [m × 2, 30 H, C$_6$H$_5$], 7.83 [ddt, 1 H, Hα, J(PHα) = 1.8 Hz, J(HαHβ) = 13.8 Hz, J(HαHβ') = 6.3 Hz] ppm; ^{31}P−{^{1}H} 31.2 ppm. Anal. Found: C,65.5; H, 4.6. C$_{39}$H$_{33}$ClOP$_2$Ru requires: C, 65.4; H, 4.6. FAB-MS *m/z* (abundance) [assignment] = 689 (8) [M − CO]$^+$, 654 (12) [M − Cl − CO]$^+$, 625 [Ru(PPh$_3$)$_2$]$^+$, 363 (14) [RuPPh$_3$]$^+$, 262 (100) [HPPh$_3$]$^+$.

Synthesis of [Ru(CH=CH$_2$)(CO)(PPh$_3$)([9]aneS$_3$)]PF$_6$ (2a·PF$_6$). [Ru(CH=CH$_2$)Cl(CO)(PPh$_3$)$_2$] (**1a**) (0.25 g, 0.35 mmol) was dissolved in dichloromethane (25 mL) and then 1,4,7-trithiacyclononane (0.07 g, 0.40 mmol) added. The solution was stirred for 20 min, during which time the color of the solution became progressively paler. All solvent was then removed and diethyl ether (20 mL) added followed by ultrasonic trituration to give off-white crystals. These were isolated by filtration, washed with diethyl ether (10 mL) and petroleum ether (10 mL), and then dried *in vacuo*. The material thus obtained was shown to be spectroscopically pure; however, metathesis of the chloride counteranion for PF$_6^-$ can be carried out by recrystallizing the crude material from a mixture of dichloromethane, ethanol, and water containing 2−3 equiv of K[PF$_6$]. IR: (Nujol) 1970vs [ν(CO)], 1556w [ν(C=C)], 1312vw, 1300vw, 1255w, 840vs [ν(PF)] cm^{-1}; (CH$_2$Cl$_2$) 1978vs [ν(CO)], 1559w [ν(C=C)] cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H δ 1.84, 2.18, 2.43, 2.80, 3.15 [m × 5, 12 H, SCH$_2$], 5.45 [dd, 1 H, Hβ, J(HαHβ) = 17.8 Hz, J(H$\beta\beta'$) = 1.7 Hz], 5.90 [ddd, 1 H, Hβ', J(HαHβ') = 10.2 Hz, J(PHβ') ≈ J(HβHβ') = 1.7 Hz], 6.95 [ddd, 1 H, Hα, J(PHα) = 6.9 Hz, J(HαHβ) = 17.5 Hz, J(HαHβ') = 10.2 Hz]; ^{31}P−{^{1}H} 40.3 ppm; ^{13}C−{^{1}H} (CDCl$_3$: CH$_2$Cl$_2$ 1:4) 198.7 [d, CO, J(PC) = 16.1 Hz], 148.0 [d, RuCH, J(PC) = 10.7 Hz], 133.8 [d, C^{3,5}(C$_6$H$_5$), J(PC) = 9.0 Hz], 131.7 [d, C^1(C$_6$H$_5$), J(PC) = 46.4 Hz], 131.0 [s, C^4(C$_6$H$_5$)], 128.6 [d, C^{2,6}(C$_6$H$_5$), J(PC) = 10.8 Hz], 127.6 [s, =CH$_2$], 35.9, 34.8, 34.3, 34.2, 32.9, 32.7 [s × 6, SCH$_2$] ppm. Anal. Found: C, 43.3; H, 4.0. C$_{27}$H$_{30}$F$_6$OP$_2$RuS$_3$ requires: C, 43.6; H, 4.1. FAB-MS: *m/z* (abundance) [assignment] = 599 (100) [M]$^+$, 571 (4) [M − vinyl]$^+$, 542 (4) [M − vinyl − CO]$^+$, 515 (16) [M − vinyl − CO − C$_2$H$_4$]$^+$, 459 (6) [M − vinyl − CO − 3(C$_2$H$_4$)]$^+$.

Synthesis of [Ru(CH=CHC$_6$H$_4$Me-4)(CO)(PPh$_3$)([9]aneS$_3$)]X [X = Cl (2b·Cl), AsF$_6$,(2b·AsF$_6$), BF$_4$ (2b·BF$_4$)]. (a) A dark red solution of 1,4,7-trithiacyclononane (0.04 g, 0.22 mmol) and [Ru(CH=CHC$_6$H$_4$Me-4)Cl(CO)(PPh$_3$)$_2$] (**1b**) (0.20 g, 0.22 mmol) in dichloromethane (20 mL) was stirred for 90 m during which time the solution decolorized to pale yellow. Addition of a solution of Na[AsF$_6$] (0.10 g, 0.47 mmol) in water (1.0 mL) and ethanol (30 mL) followed by concentration (rotary evaporator) of the solution to *ca.* 15 mL provided pale yellow crystals of the desired product. Yield: 0.14 g (80%). The corresponding chloride salt was obtained by omitting the addition of Na[AsF$_6$] and had all spectroscopic data associated with the complex identical to those for the less soluble AsF$_6$ salt.

(b) A solution of [RuH(NCMe)$_2$(CO)(PPh$_3$)$_2$]BF$_4$ (0.41 g, 0.50 mmol) in dichloromethane (30 mL) was treated with 4-ethynyltoluene (0.3 mL) and warmed gently for 2 min. The colorless solution was then treated with 1,4,7-trithiacyclononane (0.10 g, 0.55 mmol), stirred for 20 min, and then diluted with ethanol (30 mL). Concentration of the mixture afforded pale cream crystals of the salt (**2b·BF$_4$**). Yield: 0.32 g (83%).

(c) A suspension of [RuHCl(CO)(PPh$_3$)$_3$] (0.58 g, 0.50 mmol) in dichloromethane (20 mL) was treated with 4-ethynyltoluene (0.3 mL, excess) and heated under reflux for 1 min. The resulting red solution was then treated with 1,4,7-trithiacyclononane (0.10 g, 0.55 mmol) followed by a solution of NH$_4$[PF$_6$] (0.16 g, 1.0 mmol) in water (0.5 mL) and ethanol 15 mL. Following decolorization, the mixture was concentrated (rotary evaporator) to afford pale yellow crystals of the salt (**2b·PF$_6$**). Yield: 0.32 g (76%). IR: (Nujol) 1970vs [ν(CO)], 936w cm^{-1}; (CH$_2$Cl$_2$) 1976vs [ν(CO)] cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H δ 1.70, 2.10, 2.59, 2.82, 2.96, 3.13 [m × 6, 12 H, SCH$_2$], 2.27 [s, 3 H, CH$_3$], 6.54 [d, 1 H, Hβ, J(HαHβ) = 16.9 Hz], 6.96, 6.78 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) = 8.0 Hz], 7.29 [dd, 1 H, Hα, J(HαHβ) = 16.9 Hz, J(PHα) = 6.8 Hz], 7.51−7.40 [m, 15 H, C$_6$H$_5$] ppm; ^{13}C−{^{1}H} not sufficiently soluble; ^{31}P−{^{1}H} 40.6 ppm. Anal. Found: C, 46.0, H, 4.0. C$_{34}$H$_{36}$AsF$_6$OPRuS$_3$ requires: C, 46.5; H, 4.1. FAB-MS: *m/z* (abundance) [assignment] = 689 (40) [M]$^+$, 515 (10) [M − [9]aneS$_3$]$^+$.

Synthesis of [Ru(CPh=CHPh)(CO)(PPh$_3$)([9]aneS$_3$)]PF$_6$ (2c·PF$_6$). (a) A suspension of [RuHCl(CO)(PPh$_3$)$_3$] (0.47 g, 0.50 mmol) and diphenylacetylene (0.30 g, 1.70 mmol) in tetrahydrofuran (25 mL) was heated under reflux for 20 m. The solution was allowed to cool, treated with 1,4,7-trithiacyclononane (0.09 g, 0.50 mmol), and heated to reflux for 5 m. The solution was allowed to cool and then treated with a solution of NH$_4$[PF$_6$] (0.20, 1.22 mmol) in water (1.0 mL) and ethanol (20 mL). Concentration of the mixture under reduced pressure provided pale green crystals of the title complex. Yield 0.30 g (63%). This material was spectroscopically pure; however, an analytically pure sample of a dichloromethane disolvate was obtained by recrystallization twice from a mixture of dichloromethane and ethanol.

(b) **2c·AsF$_6$**. A suspension of [Ru(CPh=CHPh)Cl(CO)(PPh$_3$)$_2$] (**1c**) (0.20 g, 0.25 mmol) and 1,4,7-trithiacyclononane (0.05 g, 0.28 mmol) in tetrahydrofuran (20 mL) was heated under reflux for 2 h during which time the solution turned pale yellow. A solution of Na[AsF$_6$] (0.10 g, 1.3 mmol) in water (1.0 mL) and ethanol (20 mL) was added to the hot solution, which was then concentrated under reduced pressure to *ca.* 15 mL and cooled to 0 °C to effect the formation of cream microcrystals. Yield: 0.19 g (80%). IR: (Nujol) 1975sh, 1956vs [ν(CO)], 1592w [ν(C=C)], 1310w, 1299w, 836 [ν(PF)] cm^{-1}; (CH$_2$Cl$_2$) 1975vs [ν(CO)], 1594w [ν(C=C)] cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H δ 0.86, 1.23, 1.60, 2.36, 2.61, 2.83, 3.08, 3.22 [m × 8, 12 H, SCH$_2$], 6.03 [s(br), 1 H, =CHPh], 6.30 [d, 2

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[9] Torres, M. R.; Vegas, A.; Santos, A. *J. Organomet. Chem.* **1986,** *309* 169. Harris, M. C. J.; Hill, A. F. *Ibid.* **1992**, *438*, 209.

[10] For a recent review of the hydroruthenation of alkynes and σ-vinyl complexes of ruthenium see: Hill, A. F. In *Comprehensive Organometallic Chemistry II;* Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 7.

[11] Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1977**, *142*, C1. Rickard, C. E. F.; Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *Ibid.* **1990**, *389*, 375.

[12] Laing, K. R.; Roper, W. R. *J. Chem. Soc. A* **1970**, 2149.

[13] Cavit, B. E.; Grundy, K. R.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1972**, 60.

[14] (a) Hill, A. F.; Melling, R. P. *J. Organomet. Chem.* **1990**, *396*, C22. (b) Hill, A. F.; Harris, M. C. J.; Melling, R. P. *Polyhedron* **1992**, *11*, 781.

H, H^{2,6}(CC$_6$H$_5$), J(HH) = 6.6 Hz], 6.88, 7.11, 7.21, 7.48 [m × 4, 23 H, C$_6$H$_5$] ppm; ^{31}P−{^{1}H} 38.7 ppm; ^{13}C−{^{1}H} not sufficiently soluble. Anal. Found for chloride salt: C, 51.7; H, 4.5. $C_{39}H_{38}ClOPRuS_3\cdot 2CH_2Cl_2$ requires: C, 51.5; H, 4.4. Solvent of crystallization by NMR integration. Anal. Found for hexafluoroarsenate salt: C, 49.9; H, 4.1. $C_{39}H_{38}AsF_6OPRuS_3$ requires: C49.8; H, 4.1. FAB-MS: *m/z* (abundance) [assignment] = 751 (100) [M]$^+$, 571 (5) [M − vinyl]$^+$, 543 (3) [M − vinyl − CO]$^+$, 515 (11) [M − CO − vinyl − C$_2$H$_4$]$^+$, 461 (8) [M − CO − PPh$_3$]$^+$, 433 (32) [M − CO − C$_2$H$_4$ − PPh$_3$]$^+$, 263 (8) [HPPh$_3$]$^+$.

Synthesis of [Ru{C(C≡CPh)═CHPh}(CO)(PPh$_3$)([9]aneS$_3$)]PF$_6$ (2d·PF$_6$). [Ru{C(C≡CPh)═CHPh}Cl(CO)(PPh$_3$)$_2$] (**1d**) (0.30 g, 0.337 mmol) and 1,4,7-trithiacyclononane (0.07 g, 0.40 mmol) were dissolved in dichloromethane (20 mL) and the mixture stirred for 24 h. During this period the solution became much lighter in color, and all solvent was then removed. Ultrasonic trituration in diethyl ether (25 mL) provided a cream-colored solid that was filtered, washed with diethyl ether (20 mL) and petroleum ether (10 mL), and dried. Yield: 0.25 g (92%). The material thus obtained was shown to be spectroscopically pure; however, metathesis of the chloride counteranion for PF$_6^-$ can be carried out by recrystallizing the crude material from a mixture of dichloromethane, ethanol, and water containing 2−3 equiv of NH$_4$[PF$_6$]. IR: (Nujol) 2157w [ν(C≡C)], 1973vs [ν(CO)] 1593 [ν(C═C)], 1298w, 915w, 838vs [ν(PF)] cm^{-1}; (CH$_2$Cl$_2$) 2162vw [ν(C≡C)], 1982vs [ν(CO)] , 1594w [ν(C═C)] cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H δ 1.80, 2.12, 2.84, 3.22, 3.59, 3.77 [m × 6, 12 H, SCH$_2$], 6.62 [s(br), 1 H, Hβ], 7.08−7.6 [m, 25 H, PC$_6$H$_5$ and CC$_6$H$_5$] ppm; ^{31}P−{^{1}H} 38.8 ppm; ^{13}C−{^{1}H} 198.2 [d, CO, J(PC) = 17.9 Hz], 146.6 [s, Ru*C*═C], 139.6 [C^1(≡CC$_6$H$_5$)], 133.7 [d, C^{3,5}(PC$_6$H$_5$), J(PC) = 8.9 Hz], 131.8 [d, C^1(PC$_6$H$_5$), J(PC) = 46.4 Hz], 130.9 [C^4(PC$_6$H$_5$)], 128.6 [d, C^{2,6}(PC$_6$H$_5$), J(PC) = 10.7 Hz], 128.4, 127.8, 127.4 [C^{2,3,5,6}(CC$_6$H$_5$)], 127.6 [RuC═*C*H], 126.2 [C^1(═CHC$_6$H$_5$)], 126.2, 124.7 [C^4(C$_6$H$_5$)], 101.3, 99.4 [C≡C], 37.5, 36.9, [s × 2, SCH$_2$], 35.7[s(br), SCH$_2$, S *trans* to P], 35.3 [d, SCH$_2$, S *trans* to P, J(PC) = 7.7 Hz], 34.3, 32.1 [s × 2, SCH$_2$] ppm. Anal. Found: C, 52.6; H, 4.1. $C_{41}H_{38}F_6OP_2RuS_3\cdot 0.25CH_2Cl_2$ requires: C, 52.6; H, 4.1. Solvent of crystallization by NMR integration. FAB-MS: *m/z* (abundance) [assignment] = 775 (100) [M]$^+$, 571 (3) [M − vinyl]$^+$, 516 (9) [M − PPh$_3$]$^+$, 486 (4) [M − CO − PPh$_3$]$^+$, 457 (28) [M − CO − PPh$_3$ − C$_2$H$_4$]$^+$.

Synthesis of [Ru(C$_6$H$_4$Me-4)(CO)(PPh$_3$)([9]aneS$_3$)]PF$_6$ (2e·PF$_6$). A suspension of [Ru(C$_6$H$_4$Me-4)Cl(CO)(PPh$_3$)$_2$] (**1e**) (0.40 g, 0.51 mmol) in dichloromethane (40 mL) and ethanol (20 mL) was treated with 1,4,7-trithiacyclononane (0.10 g, 0.57 mmol) and K[PF$_6$] (0.19 g, 1.0 mmol) dissolved in water (1.0 mL) and ethanol (5 mL). The mixture was stirred for 2 h, during which time a cloudy precipitate (KCl) formed from the yellow solution. The solvent was removed under reduced pressure and the residue triturated ultrasonically with diethyl ether. The ether washings were discarded, and the residue was dissolved in dichloromethane (30 mL) . The solution was filtered through diatomaceous earth and the filtrate diluted with ethanol (30 mL). The solution was concentrated under reduced pressure to *ca.* 10 mL to effect the formation of colorless microcrystals of the desired salt, which were isolated by filtration, washed with ethanol (5 mL) and light petroleum (2 × 10 mL), and dried in vacuo. Yield: 0.25 g (61%). Further material could be obtained by concentration of the filtrate. IR: (Nujol) 1974vs [ν(CO)], 840 [ν(PF)] cm^{-1}; (CH$_2$Cl$_2$) 1976vs [ν(CO)] cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H δ 1.64, 2.17, 2.56−3.37 [m × 3] 12 H, SCH$_2$], 2.15 [s, 3 H, CH$_3$], 6.58, 6.92 [m(br) × 2, 4 H, C$_6$H$_4$-fluxional], 7.17−7.68 [m × 4, 30 H, C$_6$H$_5$] ppm; ^{13}C−{^{1}H} 198.6 [d, CO, J(PC) = 17.8 Hz], 143.6 [d, C^1(C$_6$H$_4$), J(PC) = 10.7 Hz], 142.0 [s(br), C^{2,6}(C$_6$H$_4$)], 133.8 [d, C^{3,5}(C$_6$H$_5$), J(PC) = 8.9 Hz], 132.1 [s, C^4(C$_6$H$_4$)], 131.7 [d, C^1(C$_6$H$_5$), J(PC) = 46.6 Hz], 130.9 [s, C^4(C$_6$H$_5$)], 129.0 [s, C^{3,5}(C$_6$H$_4$)], 128.6 [d, C^{2,6}(C$_6$H$_5$), J(PC) = 10.8 Hz], 38.0, 36.9, 31.8, 31.5 [s × 4, SCH$_2$], 35.6 [d, SCH$_2$,S-*trans* to P, J(PC) = 7.9 Hz], 32.5 [d, SCH$_2$, S trans to P, J(PC) = 3.6 Hz], 20.6 [CH$_3$] ppm; ^{31}P−{^{1}H} 40.4 ppm. Anal. Found: C, 46.8; H, 4.2. $C_{32}H_{34}F_6OP_2RuS_3\cdot 0.25CH_2Cl_2$ requires: C, 46.7; H, 4.2.

Crystallographic Analysis. Crystals of (**2a·PF$_6$**)·2CH$_2$Cl$_2$ suitable for diffraction analysis were grown by slow diffusion of a solution of the complex in dichloromethane into ethanol.

Crystal data for (**2a·PF$_6$**)·2CH$_2$Cl$_2$, $C_{27}H_{30}F_6OP_2RuS_3\cdot 2CH_2Cl_2$: M = 913.6, triclinic, space group $P\bar{1}$, a = 10.208(3) Å, b = 11.685(3) Å, c = 16.162(3) Å, α = 99.61(2)°, β = 104.01(2)°, γ = 93.32(2)°, V = 1834.5(7) Å^3, Z = 2, D_c = 1.654 g cm^{-1}, μ(Mo−Kα) = 10.3 cm^{-1}, F(000) = 920. A pale yellow prismatic block of dimensions 0.50 × 0.43 × 0.27 mm was used, coated with epoxy resin to inhibit desolvation.

Data Collection and Processing. Data were measured on a Siemens P4/PC diffractometer with Mo Kα radiation (graphite monochromator) using ω-scans. A total of 4760 independent reflections were measured ($2\theta \leq 45°$), of which 4163 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. These data were corrected for Lorentz and polarization factors, but not for absorption.

Structure Analysis and Refinement. The structure was solved by the heavy atom method. All the non-hydrogen atoms were refined anisotropically, all phenyl rings being treated as idealized rigid bodies. The PF$_6^-$ counteranion was found to be disordered: Two discrete 50% occupancy orientations with a common F−P−F axis were identified. The positions of all the hydrogen atoms were located from a ΔF map; all of these positions were subsequently idealized, assigned isotropic thermal parameters [U(H) = 1.2 Ueq(C)] and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least-squares methods based on F^2 to give for the observed data R_1 = 0.038, wR$_2$ = 0.094 for 415 parameters. The maximum and minimum residual electron densities in the final ΔF map were 0.50 and −0.43 eÅ^{-3}, respectively. The mean and maximum shift/error ratios in the final refinement cycle were 0.002 and 0.033, respectively. Computations were carried out on a 90 MHz Pentium PC using the SHELXTL PC program system (Version 5.03, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994). Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The σ-vinyl complexes [Ru(CR═CHR′)Cl(CO)(PPh$_3$)$_2$][10] are readily prepared for a wide range of substituents R and R′ by reaction of [RuHCl(CO)(PPh$_3$)$_3$] with alkynes RC≡CR′,[9] diynes (R = C≡CR′),[14] vinyl [Hg(CR═CHR′)$_2$],[11] or dialkynyl mercurials (R = C≡CR′).[14] These complexes, and the σ-aryl analogue [Ru(C$_6$H$_4$Me-4)Cl(CO)(PPh$_3$)$_2$],[11] by virtue of their coordinative unsaturation, readily coordinate a wide range of monodentate,[15] bidentate,[16] and tridentate[17] ligands as well as being intermediates in the hydrosulfination of alkynes

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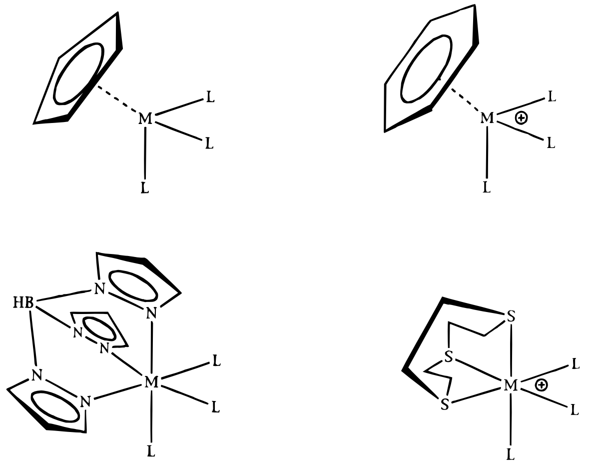
(15) Harris, M. C. J.; Hill, A. F. *Organometallics* **1991**, *10*, 3903. Hill, A. F.; Melling, R. P.; Thompsett, A. R. *J. Organomet. Chem.* **1991**, *402*, C8. Herberhold, M.; Hill, A. F. *Ibid.* **1986**, *315*, 105. Herberhold, M.; Hill, A. F. *Ibid.* **1988**, *353*, 249. Herberhold, M.; Hill, A. F. *Ibid.* **1989**, *377*, 151. Herberhold, M.; Hill, A. F. *Ibid.* **1990**, *395*, 327. Hill, A. F. *J. Chem. Soc., Chem. Commun.* **1995**, 741. Alcock, N. W.; Cartwright, J.; Hill, A. F.; Marcellin, M.; Rawles, H. M. *Ibid.* **1995**, 369. Gieren, A.; Ruiz-Perez, C.; Hübner, T.; Herberhold, M.; Hill, A. F. *J. Chem. Soc., Dalton Trans.* **1988**, 1693. Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. *J. Organomet. Chem.* **1987**, *326*, 413. Torres, M. R.; Santos, A.; Perales, A.; Ros, J. *Ibid.* **1988**, *353*, 221. Torres, M. R.; Perales, A.; Loumrhari, H.; Ros, J. *Ibid.* **1990**, *384*, C61. Montoya, J.; Santos, A.; Echavarren, A. M.; Ros, J. *Ibid.* **1990**, *390*, C57. Loumrhari, H.; Ros, J.; Yanez, R.; Torres, M. R. *Ibid.* **1991**, *408*, 233. Loumrhari, H.; Ros, J.; Torres, M. R.; Santos, A.; Echavarren, A. M. *Ibid.* **1991**, *411*, 255. Montoya, J.; Santos, A.; Lopez, J.; Echavarren, A. M.; Ros, J.; Romero, A. *Ibid.* **1992**, *426*, 383. Torres, M. R.; Perales, A. Ros, J. *Organometallics* **1988**, *7*, 1223.

Chart 1. Coordination of 1,4,7-Trithiacyclononane [9]aneS$_3$ and Related Facially Tridentate Ligands

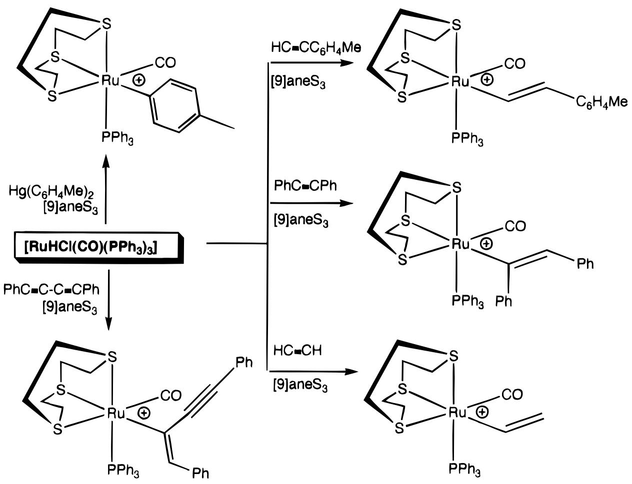


by $[RuHCl(CO)(PPh_3)_3]$.[18] We have recently been concerned with the addition of polydentate ligands and found that they provided a facile access to a range of σ-organylhydrotris(pyrazolyl)borato complexes of ruthenium(II), $[Ru(CR{=}CHR')(CO)(PPh_3)\{HB(pz)_3\}]$ (pz = pyrazol-1-yl).[17] The facial tridentate coordination of 1,4,7-trithiacyclononane ([9]aneS$_3$) to a metal is in some ways reminiscent of the coordination of cyclopentadienyl, arene, or hydrotris(pyrazolyl)borate ligands (Chart 1).

The reactions of $[Ru(CR{=}CHR')Cl(CO)(PPh_3)_2]$ (**1**) with [9]aneS$_3$ were therefore investigated. For these purposes we chose three representative vinyl ligands: unsubstituted (**1a**), *trans*-β-monosubstituted (**1b**), and α,β-disubstituted (**1c**). The parent vinyl complex $[Ru(CH{=}CH_2)Cl(CO)(PPh_3)_2]$ (**1a**) has been described as forming in a mixture with poly-unsaturated vinyl derivatives $[Ru\{(CH{=}CH)_nCH{=}CH_2\}Cl(CO)(PPh_3)_2]$ from the reaction of $[RuHCl(CO)(PPh_3)_3]$ with ethyne. In our hands this was not observed to be the case, and high yields of pure (**1a**) are obtained by judicious control of reaction time and the amount of ethyne used (see Experimental Section).

Addition of [9]aneS$_3$ to a bright red solution of $[Ru(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$ (**1b**) leads to decolorization and the formation of a product formulated as the salt $[Ru(CH{=}CHC_6H_4Me\text{-}4)(CO)(PPh_3)([9]aneS_3)]$-Cl (**2b·Cl**). Spectroscopic data for this material are essentially identical to those of the more crystalline compounds obtained by counterion metathesis with $Li[ClO_4]$, $NH_4[PF_6]$, or $Na[AsF_6]$. In a similar manner the reactions of $[RuRCl(CO)(PPh_3)_2]$ [R = $CH{=}CH_2$ (**1a**), $CPh{=}CHPh$ (**1c**)] with [9]aneS$_3$ and $NH_4[PF_6]$ provide the salts $[RuR(CO)(PPh_3)([9]aneS_3)]PF_6$ (R = $CH{=}CH_2$ (**2a·PF$_6$**), $CPh{=}CHPh$ (**2c·PF$_6$**)] (Scheme 1). The complexes are thermally and aerobically stable as solids or briefly stable in solution. The formulations rest on spectroscopic data and an X-ray diffraction analysis of the bis(dichloromethane) solvate of **2a·PF$_6$** (vide infra): The gross molecular composition follows from elemental microanalytical and FAB-MS data. These include, in addition to a correctly distributed isotope cluster for the molecular ion, fragmentations attributable to loss of the macrocyclic, carbonyl, vinyl, and phosphine ligands. The appearance of one ν(CO)-associated infrared absorption [(Nujol) 1970 cm^{-1} (**2b·PF$_6$**)] indicates that migratory insertion of the alkenyl and carbonyl ligands has not occurred. ^{1}H NMR data associated with the macrocycle ligand in the complexes are complicated (up to nine multiplets) due to the chirality at ruthenium rendering all 12 macrocycle proton environments chemically inequivalent. These data will be dealt with in more detail later (vide infra), however, data associated with the vinyl ligand are typical for such a ligand being bound *trans* to a good donor ligand: The proton α to ruthenium in **2b**$^+$ appears as a double-doublet (δ 7.29 ppm) showing *trans* coupling to one proton (16.9 Hz) and one phosphorus (6.8 Hz). The β-proton, however only shows resolvable coupling to the α-proton. The ^{13}C NMR data for the complexes further confirm the formulations: The carbonyl ligand in **2a**$^+$ gives rise to a doublet (198.7 ppm) showing a typical *cis* PRuCO coupling of 16.1 Hz, while the C$_\alpha$ resonance for the vinyl ligand appears as a doublet [J(PC) = 10.7 Hz] at 148.0 ppm. The six carbon atoms of the macrocycle are chemically distinct and give rise to six peaks in the region 10−40 ppm. For **2a**$^+$ these appear as singlets; however, in this and related examples two of these are either broad or resolved into doublets. For example, in the case of the 4-tolyl derivative $[Ru(C_6H_4Me\text{-}4)(CO)(PPh_3)([9]aneS_3)]PF_6$ (**2e·PF$_6$**) (vide infra) two doublets are clearly seen with couplings to phosphorus of 7.9 and 3.6 Hz. In all the spectra the two broadened or split resonances are therefore attributed to the (diastereotopic) methylene carbons bound to the sulfur atom *trans* to phosphorus.

Scheme 1. Synthesis of σ-Hydrocarbyl [9]aneS$_3$ Complexes



We have recently been concerned with the coordination chemistry of α-alkynyl vinyl ligands bound to ruthenium, osmium, and rhodium and have prepared the complex $[Ru\{C(C{\equiv}CPh){=}CHPh\}(CO)(PPh_3)\{\kappa^3\text{-}HB(pz)_3\}]PF_6$ *via* the reaction of $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$ (**1d**) with $K[HB(pz)_3]$.[17] In a similar manner to the synthesis of **2a**−**2c**, the reaction of

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[16] Cartwright, J.; Hill, A. F. *J. Organomet. Chem.* **1992**, *429*, 229. Hector, A. L.; Hill, A. F. *Ibid.* **1993**, *447*, C7. Cartwright, J.; Harman, A.; Hill, A. F. *Ibid.* **1990**, *396*, C31. Burns, I. D.; Hill, A. F.; Thompsett, A. R.; Alcock, N. W.; Claire, K. S. *Ibid.* **1992**, *425*, C8. Torres, M. R.; Perales, A.; Loumrhari, H.; Ros, J. *Ibid.* **1990**, *385*, 379. Loumrhari, H.; Matas, L.; Ros, J.; Torres, M. R.; Perales, A. *Ibid.* **1991**, *403*, 373. Santos, A.; Lopez, J.; Montoya, J.; Noheda, P.; Romero, A.; Echavarren, A. M. *Organometallics* **1994**, *13*, 3605. Loumrhari, H.; Ros, J.; Torres, M. R. *Polyhedron* **1991**, *10*, 421. Loumrhari, H.; Ros, J.; Torres, M. R.; Perales, A. *Ibid.* **1990**, *9*, 907.

[17] Alcock, N. W.; Hill, A. F.; Melling, R. P. *Organometallics* **1991**, *10*, 3898. Hill, A. F. *J. Organomet. Chem.* **1990**, *385*, C35.

[18] Hill, A. F. *J. Chem. Soc., Chem. Commun.* **1995**, 741.

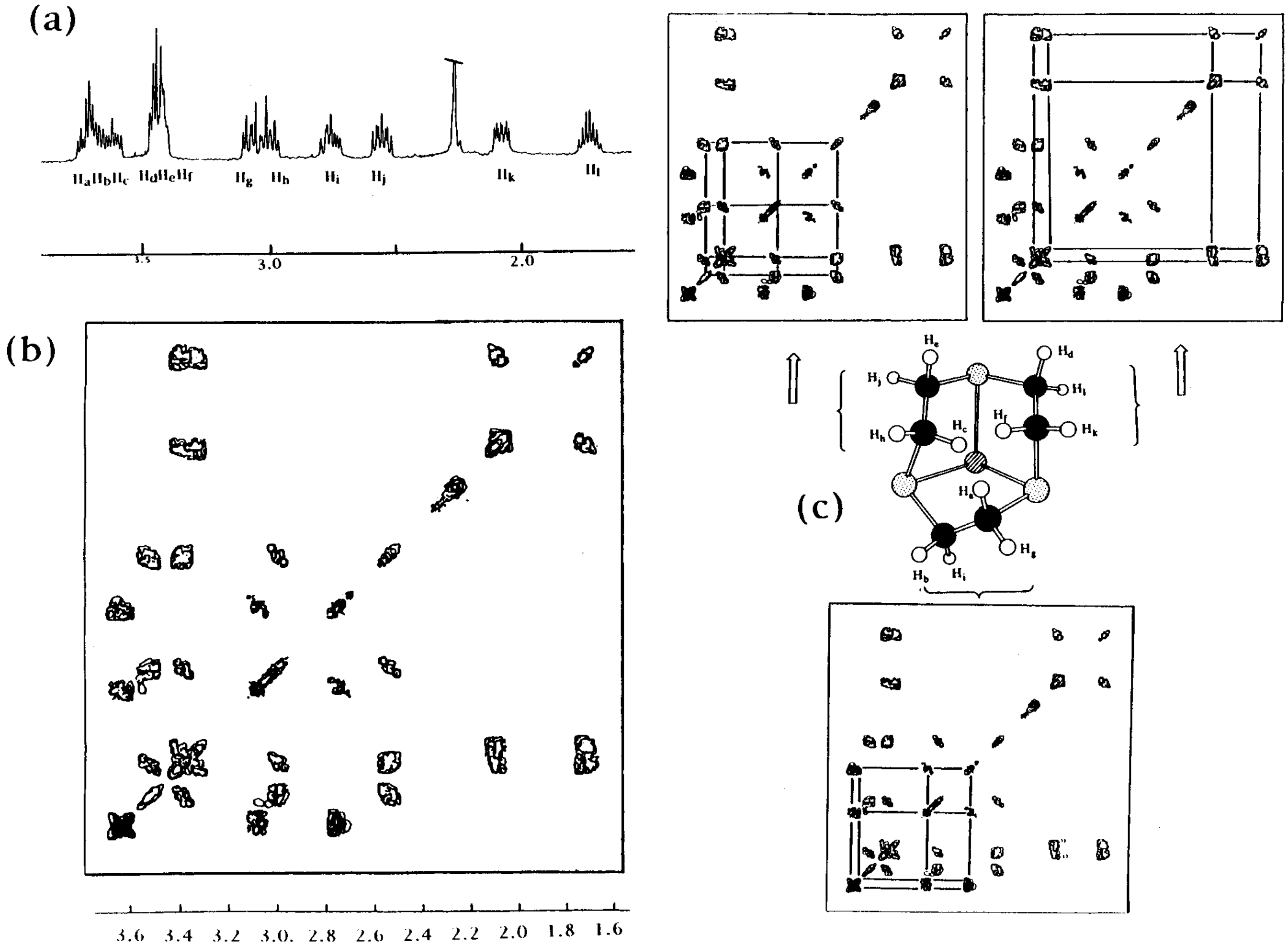

Figure 2. NMR spectroscopic analysis of [Ru(CH=CHC$_6$H$_4$Me-4)CO)(PPh$_3$)([9]aneS$_3$)]Cl. (a) 1-D ^{1}H NMR spectrum in the region δ 1.6−3.8 ppm (CH$_3$ resonance augmented). (b) 2D-(^{1}H−^{1}H) COSY NMR spectrum in the region δ 1.6−3.8 ppm. (c) Illustration of the three distinct ethylene coupling systems as a result of coordination of [9]aneS$_3$ to a chiral ruthenium centre.

1d with [9]aneS$_3$ and NH$_4$[PF$_6$] provides [Ru{C(C≡CPh)=CHPh}(CO)(PPh$_3$)([9]aneS$_3$)]PF$_6$ (**2d·PF$_6$**). In contrast to the simple vinyl derivatives, this complex is yellow; however, all spectroscopic data indicate that it is of the same general structure. The possibility that the sulfur macrocycle is bidentate with the enynyl ligand adopting a *trihapto* coordination may be excluded by the observation of a peak at 2157 cm^{-1} in the infrared spectrum that is attributable to the free alkynyl group. Furthermore, the acetylenic carbons give rise to singlet resonances in the ^{13}C−{^{1}H} NMR spectrum at 101.3 and 99.4 ppm. The absence of coupling to phosphorus would therefore appear to also preclude coordination to the ruthenium centre.

The reactions of [RuHCl(CO)(PPh$_3$)$_3$] with alkynes are in many cases sufficiently clean that it is not necessary to preisolate the coordinatively unsaturated σ-vinyl complexes. Thus, treating [RuHCl(CO)(PPh$_3$)$_3$] with a terminal alkyne (RC≡CH: R = H, C$_6$H$_4$Me-4; 2−3 equiv) in dichloromethane followed by [9]aneS$_3$ and Cl/PF$_6$ metathesis provides the salts **2a·PF$_6$** and **2b·PF$_6$** in overall yields comparable to those obtained from the isolated σ-vinyl complexes **1a** and **1b**. In the case of internal alkynes (PhC≡CPh, PhC≡CC≡CPh), the same approach is successful with the exception that hydroruthenation is normally less facile and refluxing tetrahydrofuran is required prior to addition of [9]aneS$_3$ and NH$_4$[PF$_6$] to provide **2c·PF$_6$** and **2d·PF$_6$**. The salt [RuH(CO)(NCMe)$_2$(PPh$_3$)$_2$]BF$_4$ has been shown[19] to provide σ-vinyl complexes [Ru(CH=CHR)(CO)(NCMe)$_2$(PPh$_3$)$_2$]$^+$ the nitrile ligands of which are labile and readily replaced by bidentate ligands.[16] These complexes can be generated *in situ* and also serve as precursors for [9]aneS$_3$ coordination. Thus, treating [RuH(CO)(NCMe)$_2$(PPh$_3$)$_2$]BF$_4$ with 2 equiv of a terminal alkyne followed by [9]aneS$_3$ provides the salts **2a·BF$_4$** and **2b·BF$_4$** and precludes the requirement of counteranion metathesis.

The 16-electron σ-aryl complex [Ru(C$_6$H$_4$Me-4)Cl(CO)(PPh$_3$)$_2$] (**1e**) is readily available from the reaction of [RuHCl(CO)(PPh$_3$)$_3$] with [Hg(C$_6$H$_4$Me-4)$_2$].[10] Treating **1e** with [9]aneS$_3$ and NH$_4$[PF$_6$] provides the air-stable colorless salt [Ru(C$_6$H$_4$Me-4)(CO)(PPh$_3$)([9]aneS$_3$)]PF$_6$ in 61% yield. In contrast to the precursor complex, the salt shows no tendency to react with carbon monoxide via migratory insertion, consistent with the coordinative saturation at ruthenium. This observation, while not surprising, does confirm that the macrocyclic ligand, once coordinated, does not dissociate any of its sulfur donors to an extent sufficient to allow CO coordination. Spectroscopic data for **2e**$^+$ are essentially comparable

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(19) López, J.; Romero, A.; Santos, A.; Vegas, A.; Echavarren, A. M.; Noheda, P. *J. Organomet. Chem.* **1989**, *373*, 249.

to those for the σ-vinyl derivatives $\mathbf{2a}^+$−$\mathbf{2d}^+$ with two exceptions: Firstly, both the tolyl $(AB)_2$ "quartet" resonance in the ^1H NMR spectrum and the resonance due to the *o*-tolyl carbons in the ^{13}C NMR spectrum are broad, indicating presumably that the molecule is fluxional. The nature of this fluxionality is therefore associated with rotation of the tolyl group about the Ru−C bond. Secondly, the resonances due to the (diastereotopic) methylene carbons bound to sulfur trans to phosphorus are clearly resolved into two doublets with different couplings to phosphorus.

Further NMR Studies. As noted above, the NMR data associated with the macrocycle in salts of the complexes $\mathbf{2}^+$, while indicating the low symmetry of the ruthenium coordination sphere, are not particularly informative. The data do, however, indicate that the macrocycle does not dissociate on the ^1H-NMR time scale. It is, however, noteworthy that the various multiplets associated with the [9]aneS_3 ring span a range of over 2 ppm as shown in the representative spectrum of **2b·Cl** shown in Figure 2a. We therefore chose to investigate one example in more detail using two-dimensional $^1H-^1H$ COSY-45 techniques. For this purpose, the chloride salt **2b·Cl** was used as the salts of the noncoordinating anions were insufficiently soluble. The 2D-COSY-45 spectrum in the range 1.6−3.7 ppm is shown in Figure 2b. Using both the occurrence of off-diagonal peaks and the direction of the contour lines of each of the peaks it is possible to identify and to distinguish ^2J and ^3J couplings. Thus, it is possible to divide the spectrum into three sets of mutually coupled ABCD spin systems corresponding to the three ethylene bridges of the macrocycle. This subdivision is illustrated in Figure 2c. Thus, for example, the protons H_c, H_e, H_h, and H_j can be seen to all be mutually coupled by the appearance of the off-diagonal peaks indicated. Furthermore, it can be seen that the long axis of the ovoid contours for the cross-peaks between H_j and H_h is perpendicular to the diagonal, indicating that the coupling between these two nuclei is vicinal (^3J). The direction of the long axis of the countours for the $J(H_jH_e)$ off-diagonal peak is, however, parallel to the diagonal, indicating a geminal relationship (^2J) for these two protons. More generally, it can be seen that each of the 12 proton resonances is associated with two perpendicular and one parallel off-diagonal peak, i.e., coupling to one geminal and two vicinal protons.

While this exercise was not carried out with all complexes, in this case the simplification of the data is reassuring in regard to the formulation. The facial "Ru(CO)(PPh_3)(σ-vinyl)" moiety causes a surprisingly wide spread of chemical shift values for the macrocyclic protons. This could be for two reasons. Firstly, the three ligands have very different electronic effects on the metal center. It has on occasion[20] been argued that sulfur-based macrocycles may function as π-acceptor ligands, and while this will no doubt remain a matter for debate, any such interaction could be transmitted to the adjacent CH_2 groups if S−C σ* orbitals are involved in the retrodative process. Alternatively, the coordination sphere is sterically very irregular (e.g., see Figure 4), and this might exert variable interligand nonbonding interactions. This latter possibility may be investigated by NOE experiments, and these point toward an interaction between the *ortho* protons of the phosphine rings and some but not all of the macrocycle protons. Specifically, it is the highest field proton, designated "h", that shows a through-space interaction.

Table 1. Crystal Data and Data Collection and Solution and Refinement Details for $[Ru(CH{=}CH_2)(CO)(PPh_3)([9]aneS_3)]PF_6$

	Crystal Data
emp formula	$C_{27}H_{30}OPS_3Ru{\cdot}PF_6{\cdot}2(CH_2Cl_2)$
M_r	913.55
a, b, c (Å)	10.208(3), 11.685(3), 16.162(3)
α, β, γ (deg)	99.61(2), 104.01(2), 93.32(2)
V (Å^3)	1834.5(7)
space grp	$P\bar{1}$
Z	2
D_{calcd} (g cm^{-3})	1.654
crystallizn	diffusion of ethanol into a dichloromethane solution
cryst size (mm)	0.50 × 0.43 × 0.27
	Data Collection
T (K)	293(2)
diffractometer	Siemens P4/PC
scan type	ω-scans ($3.56 \le 2\theta \le 45.0°$)
abs cor	none
no. of data	4760 unique; 4163 with $F \ge 4\sigma(F)$ retained
	Solution and Refinement
method	heavy atom and difference Fourier
program	SHELXTL PC Version 5.03
residuals	$R_1 = 0.038$, w$R_2 = 0.0943$ e density max = 0.504, min = −0.425 e Å^{-3}

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $\mathbf{2a}^+$

Ru−C(30)	1.858(5)	Ru−C(28)	2.097(5)
Ru−P	2.3469(13)	Ru−S(1)	2.3747(13)
Ru−S(4)	2.4156(13)	Ru−S(7)	2.4370(12)
P−C(27)	1.833(2)	P−C(15)	1.846(2)
P−C(21)	1.848(2)	S(1)−C(2)	1.806(6)
S(1)−C(9)	1.827(6)	C(2)−C(3)	1.478(8)
C(3)−S(4)	1.826(5)	S(4)−C(5)	1.832(6)
C(5)−C(6)	1.471(8)	C(6)−S(7)	1.798(5)
S(7)−C(8)	1.832(5)	C(8)−C(9)	1.462(8)
C(28)−C(29)	1.292(7)	C(30)−O(31)	1.137(6)
C(30)−Ru−C(28)	89.5(2)	C(30)−Ru−P	88.10(14)
C(28)−Ru−P	91.18(14)	C(30)−Ru−S(1)	89.80(14)
C(28)−Ru−S(1)	87.75(14)	P−Ru−S(1)	177.65(4)
C(30)−Ru−S(4)	172.9(2)	C(28)−Ru−S(4)	84.28(14)
P−Ru−S(4)	95.56(4)	S(1)−Ru−S(4)	86.41(5)
C(30)−Ru−S(7)	100.8(2)	C(28)−Ru−S(7)	167.82(13)
P−Ru−S(7)	95.64(4)	S(1)−Ru−S(7)	85.79(5)
S(4)−Ru−S(7)	85.02(4)	C(27)−P−Ru	114.08(11)
C(15)−P−Ru	118.33(10)	C(21)−P−Ru	115.49(9)
C(2)−S(1)−C(9)	101.8(3)	C(2)−S(1)−Ru	106.7(2)
C(9)−S(1)−Ru	102.6(2)	C(3)−S(4)−C(5)	100.8(3)
C(3)−S(4)−Ru	100.9(2)	C(5)−S(4)−Ru	106.0(2)
C(6)−S(7)−C(8)	102.5(3)	C(6)−S(7)−Ru	103.5(2)
C(8)−S(7)−Ru	104.8(2)	C(29)−C(28)−Ru	130.3(5)
O(31)−C(30)−Ru	177.2(4)		

Discussion of the Structure of $(\mathbf{2a}{\cdot}\mathbf{PF_6}){\cdot}\mathbf{2CH_2Cl_2}$. The racemic salt forms colorless crystals of a bis(dichloromethane) solvate. The results of the X-ray analysis are summarised in Tables 1 (procedural details) and 2 (selected bond lengths and angles) and Figures 3 and 4, which depict the geometry of the cationic complex $\mathbf{2a}^+$.

The X-ray analysis shows the ruthenium to have a slightly distorted octahedral coordination with angles at ruthenium in the ranges 84.3(1)−100.8(1)° and 167.8(1)−177.7(1)°. The [9]aneS_3 macrocycle is in a conventional facial perching coordination mode with intersulfur angles of 85.0(1)−86.4(1)°. The conforma-

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[20] Blake, A. J.; Holder, A. J.; Hyde, T. J.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1433.

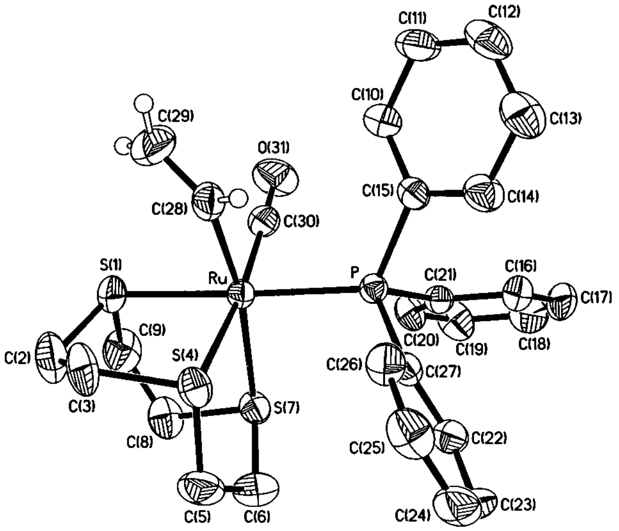

Figure 3. Molecular structure of the cation ($\mathbf{2a}^+$) of $[Ru(CH{=}CH_2)(CO)(PPh_3)([9]aneS_3)]PF_6{\cdot}2CH_2Cl_2$ showing 40% probability thermal ellipsoids.

tions of each five-membered chelate ring are either all δ or all λ depending on the enantiomer. The ruthenium–sulfur distances all differ significantly from each other with the longest Ru–S linkage [2.437(1) Å] being that *trans* to the σ-vinyl group, reflecting the strong trans influence of σ-organyl groups in general. Of intermediate length [2.416(1) Å] is the bond *trans* to the carbonyl ligand, while the shortest [2.375(1) Å] is that *trans* to the bulky phosphine. What is of note is the fact that all the Ru–S distances are noticeably longer that those normally observed for $[9]aneS_3$ complexes of divalent ruthenium. The phosphine to ruthenium distance of 2.347(1) Å is normal for six-coordinate ruthenium(II), as is the Ru–CO distance of 1.858(5) Å. The bond from ruthenium to the vinyl carbon, at 2.097(5) Å, is within the range reported[10] for vinyl complexes of divalent ruthenium. The associated C=C bond distance of 1.292(7) Å indicates a pronounced degree of bond ordering and an absence of any significant π-retrodonation from the cationic ruthenium centre. This is further supported by the ambivalent orientation of the plane of the vinyl ligand, which is inclined by *ca.* 32° to the Ru–P vector. There are no notable intermolecular interactions.

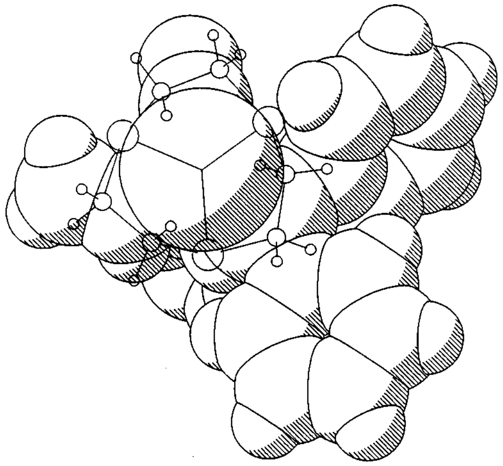

Figure 4. Partial space-filling representation of complex $\mathbf{2a}^+$ illustrating the irregularity of the steric profile of the "Ru(vinyl)(CO)(PPh_3)" fragment. The view is along the axis perpendicular to the plane defined by S(1), S(2), and S(3).

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Supporting Information Available: Tables of final atomic positional parameters and anisotropic thermal parameters for the structural analysis (7 pages). Ordering information is given on any current masthead page.

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