Synthetic and Computational Studies of Thiocarbonyl/σ-Organyl Coupling Reactions[1]

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The reactions of a range of coordinatively unsaturated σ-organyl thiocarbonyl complexes with 1,4,7-trithiacyclononane ([9]aneS$_3$) have been investigated, leading in some but not all cases to migratory insertive coupling of thiocarbonyl and σ-organyl ligands. Thus, under ambient conditions, the reaction of [RuRCl(CS)(PPh$_3$)$_2$] (R = C(CO$_2$Me)=CHCO$_2$Me, C(C≡CPh)=CHPh, C$_6$H$_5$) with [9]aneS$_3$ provides σ-organyl complexes [RuR(CS)(PPh$_3$)([9]aneS$_3$)]$^+$. On heating, the species [Ru(C$_6$H$_5$)(CS)(PPh$_3$)([9]aneS$_3$)]$^+$ converts to the thiobenzoyl complex [Ru(η^2-SCPh)(PPh$_3$)([9]aneS$_3$)]$^+$. Similarly the silyl complex [RuCl(SiMe$_2$OEt)(CS)(PPh$_3$)$_2$] with [9]aneS$_3$ provides [Ru(SiMe$_2$OEt)(CS)(PPh$_3$)([9]aneS$_3$)]$^+$. However, the styryl and stilbenyl complexes [Ru(CR=CHPh)Cl(CS)(PPh$_3$)$_2$] (R = H, Ph) under similar conditions provide dihapto thioacyl derivatives [Ru(η^2-SCCR=CHPh)(PPh$_3$)([9]aneS$_3$)]$^+$. The osmium species [Os(CH=CHC$_6$H$_4$Me-4)Cl(CS)(BTD)(PPh$_3$)$_2$] (BTD = 2,1,3-benzothiadiazole), however, yields only the nonmigrated product [Os(CH=CHC$_6$H$_4$Me-4)(CS)(PPh$_3$)([9]aneS$_3$)]$^+$. Migratory insertion is not induced by other sulfur donor ligands, e.g., Cy$_3$PCS$_2$ (Cy = cyclohexyl) and Na[S$_2$CNMe$_2$], which provide the complexes [Ru(CH=CH$_2$)(S$_2$CPCy$_3$)(CS)(PPh$_3$)$_2$]$^+$ and [Ru(CH=CHPh)(S$_2$CNMe$_2$)(CS)(PPh$_3$)$_2$], respectively. The reactivity of different ligands (R) toward thiocarbonyl migratory insertion in [Ru(R)(CS)(PPh$_3$)([9]aneS$_3$)]$^+$ was analyzed through density functional theory. The calculated barriers agree qualitatively with experimental observations. In order to determine the electronic effect of substituents on the migrating ligand, a series of hypothetical systems with phenyl ligands varying only in the *para*-substituent was considered. A general trend that electron-releasing substituents on the migrating ligand promote reaction was observed. Through symmetry-adapted fragment orbital analysis, this phenomenon is determined to correlate well with the energy of the highest occupied π-orbital of the ligand.

Introduction

Bi- and, to a lesser extent, polydentate phosphines are prevalent in many metal-mediated catalytic processes. It has long since been speculated[2] that sulfur-based macrocycles might offer promise as co-ligands in such processes by offering a combination of multiple soft donors that mimic phosphines in combination with the robust nature of macrocycle coordination. The latter might be expected to offset the general lability of monodentate thioether binding. With very few exceptions[1,3] this potential has yet to be investigated in any detail, and little is known about how polythiacycloalkanes might effect the reactivity of organometallic co-ligands. Our own efforts to address this situation have focused on 1,4,7-trithiacyclononane ([9]anS$_3$)[1,4] for the following reasons, each of which should predispose it to catalytic applications: (i) It is commercially available, though somewhat expensive; (ii) in serving as a facially tridentate six-electron donor, it may be considered as a cyclopentadienyl mimic; (iii) the remaining sites in its octahedral or five-coordinate complexes are, by necessity, mutually *cis*, and therefore preorganized for co-ligand coupling processes, e.g., insertion and migratory insertion reactions. With the exception of commercial availability, each of these points applies to the related macrocycle 3,4-benzo-[11]aneS$_3$, the similarly rich chemistry of which has been investigated Loeb.[5] Within the chemistry of ruthenium, [9]aneS$_3$ has played an increasingly important role[6] including the synthesis of organometallic complexes.[7]

The results to be described herein relate to the key organometallic process of migratory insertion and, in particular, as it

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(1) Organometallic Macrocycle Chemistry Part 7. For part 6 see: Hill, A. F.; Wilton-Ely, J. D. E. T. *Organometallics* **1997**, *16*, 4517.

(2) Cooper, S.; Rawle, S. C. *Struct. Bonding (Berlin)* **1990**, *72*, 1.

(3) (a) Adams, R. D.; Falloon, S. B. *Organometallics* **1995**, *14*, 4594. (b) Adams, R. D.; Falloon, S. B. *Organometallics* **1995**, *14*, 1748. (c) Adams, R. D.; Falloon, S. B. *J. Am. Chem. Soc.* **1994**, *116*, 10540. (d) Adams, R. D.; Cortopassi, J.; Falloon, S. J. *Organomet. Chem.* **1993**, *463*, C5. (e) Timonen, S.; Pakkanen, T. T.; Pakkanen, T. A. *J. Mol. Catal. A* **1996**, *111*, 267.

(4) (a) Cannadine, J.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1996**, *15*, 5409. (b) Hill, A. F.; Alcock, N. W.; Cannadine, J. C.; Clark, G. R. *J. Organomet. Chem.* **1992**, *426*, C40. (c) Hill, A. F.; Alcock, N. W.; Cannadine, J. C.; Clark, G. R. *J. Chem. Soc., Dalton Trans.* **1993**, 1131. (d) Hector, A. L.; Hill, A. F. *Inorg. Chem.* **1995**, *34*, 3797. (e) Cannadine, J.; Hector, A. L.; Hill, A. F. *Organometallics* **1992**, *11*, 2323. (f) Bedford, R. B.; Hill, A. F.; Jones, C.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, *17*, 4744.

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relates to thiocarbonyl ligands. In an organometallic context,[8] carbon monosulfide is in all respects except its availability[9−11]

Chart 1. Energies (eV) and Topologies of the Frontier Orbitals of CO, CS, and CNH

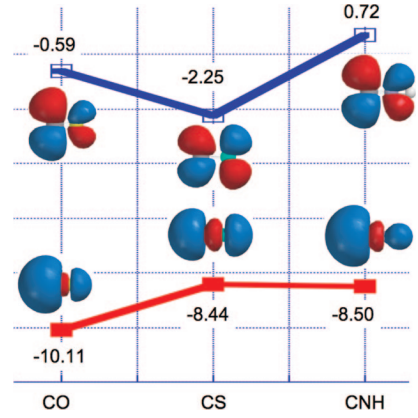
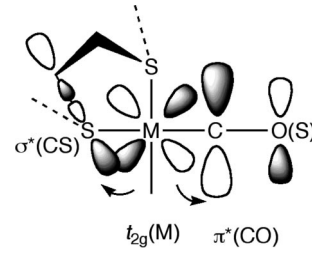


Chart 2. Supposed Competitive Retrodonation to [9]aneS$_3$ (adapted from ref 36)



a superlative isosteric surrogate for carbon monoxide. The frontier orbitals of CS[12] are topologically similar to those of CO; however the energetics are significantly different (Chart 1). Thus replacement of oxygen by sulfur stabilizes the π-acidic orbitals and destabilizes the σ-donor orbital used for binding to a transition metal; that is, CS is both a stronger σ-donor and π-acid ligand than CO. The chemical implications, beyond stronger binding to the metal, are as follows: (i) Transfer of electron density out onto the sulfur makes it more prone to electrophilic attack than CO, providing a route to thiolatocarbyne complexes.[13] (ii) For metal centers of only modest π-basicity where retrodonation fails to satisfy the electrophilicity of the π^* orbitals, the CS ligand is more prone to nucleophilic attack than CO. (iii) In binuclear carbonyl/thiocarbonyl complexes, it is always the thiocarbonyl ligand that assumes a bridging role.

It is perhaps in the area of migratory insertion (Scheme 1) that thiocarbonyls present the most dramatic reactivity. In addition to conventional σ-organyls,[16] a range of co-ligands not normally associated with migration to CO have been shown to

(5) (a) De Groot, B.; Giesbrecht, G. R.; Loeb, S. J.; Shimizu, G. K. H. *Inorg. Chem.* **1991**, *30*, 177. (b) De Groot, B.; Hanan, G. S.; Loeb, S. J. *Inorg. Chem.* **1991**, *30*, 4644. (c) De Groot, B.; Jenkins, H. A.; Loeb, S. J. *Inorg. Chem.* **1992**, *31*, 203. (d) Giesbrecht, G. R.; Hanan, G. S.; Kickham, J. E.; Loeb, S. J. *Inorg. Chem.* **1992**, *31*, 3286. (e) Jenkins, H. A.; Loeb, S. J. *Organometallics* **1994**, *13*, 1840. (f) De Groot, B.; Jenkins, H. A.; Loeb, S. J.; Murphy, S. L *Can. J. Chem.* **1995**, *73*, 1102. (g) Casabo, J.; Flor, T.; Hill, M. N. S.; Jenkins, H. A.; Lockhart, J. C.; Loeb, S. J.; Romero, I.; Teixidor, F. *Inorg. Chem.* **1995**, *34*, 5410.

(6) (a) Bratsos, I.; Birarda, G.; Jedner, S.; Zangrando, E.; Alessio, E. *Dalton Trans.* **2007**, *4*, 048. (b) Laurenczy, G.; Jedner, S.; Alessio, E.; Dyson, P. J. *Inorg. Chem. Commun.* **2007**, *10*, 558. (c) Shan, N.; Ingram, J. D.; Easun, T. L.; Vickers, S. J.; Adams, H.; Ward, M. D.; Thomas, J. A. *Dalton Trans.* **2006**, 2900. (d) Shan, N.; Adams, H.; Thomas, J. A. *Inorg. Chim. Acta* **2006**, *359*, 759. (e) Serli, B.; Zangrando, E.; Gianferrara, T.; Scolaro, S.; Dyson, P. J.; Bergamo, A.; Alessio, E. *Eur. J. Inorg. Chem.* **2005**, 3423. (f) Iengo, E.; Zangrando, E.; Baiutti, E.; Munini, F.; Alessio, E. *Eur. J. Inorg. Chem.* **2005**, 1019. (g) Maurer, P.; Magistrato, A.; Rothlisberger, U *J. Phys. Chem. A* **2004**, *108*, 11494. (h) Shan, N.; Vickers, S. J.; Adams, H.; Ward, M. D.; Thomas, J. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 3938. (i) Sala, X.; Romero, I.; Rodriguez, M.; Llobet, A.; Gonzalez, G.; Martinez, M.; Benet-Buchholz, J. *Inorg. Chem.* **2004**, *43*, 5403. (j) Adams, H.; Shan, N.; Thomas, J. *Acta Crystallograph., Sect. E: Struct. Rep. Online* **2004**, *E60*, m662. (k) Sala, X.; Poater, A.; Romero, I.; Rodriguez, M.; Llobet, A.; Solans, X.; Parella, T.; Santos, T. M. *Eur. J. Inorg. Chem.* **2004**, 612. (l) Araujo, C. S.; Drew, M. G. B.; Felix, V.; Jack, L.; Madureira, J.; Newell, M.; Roche, S.; Santos, T. M.; Thomas, J. A.; Yellowlees, L. *Inorg. Chem.* **2002**, *41*, 2250. (m) Santos, T. M.; Madureira, J.; Goodfellow, B. J.; Drew, M. G. B.; Pedrosa de Jesus, J.; Felix, V. *Metal-Based Drugs* **2001**, *8*, 125. (n) Roche, S.; Spey, S. E.; Adams, H.; Thomas, J. A. *Inorg. Chim. Acta* **2001**, *323*, 157. (o) Santana-Marques, M. G. O.; Amado, F. M. L.; Correia, A. J. F.; Lucena, M.; Madureira, J.; Goodfellow, B. J.; Felix, V.; Santos, T. M. *J. Mass Spectrom.* **2001**, *36*, 529. (p) Madureira, J.; Santos, T. M.; Goodfellow, B. J.; Lucena, M.; Pedrosa de Jesus, J.; Santana-Marques, M. G.; Drew, M. G. B.; Felix, V. *Dalton Trans.* **2000**, 4422. (q) Roche, S.; Adams, H.; Spey, S. E.; Thomas, J. A. *Inorg. Chem.* **2000**, *39*, 2385. (r) Roche, S.; Haslam, C.; Heath, S. L.; Thomas, J. A. *Chem. Commun.* **1998**, 1681. (s) Roche, S.; Thomas, J. A.; Yellowlees, L. J. *Chem. Commun.* **1998**, 1429. (t) Goodfellow, B. J.; Felix, V.; Pacheco, S. M. D.; Pedrosa de Jesus, J.; Drew, M. G. B. *Polyhedron* **1996**, *16*, 393. (u) Landgrafe, C.; Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **1996**, 989. (v) Landgrafe, C.; Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **1994**, 1885. (w) Blake, A. J.; Christie, R. M.; Roberts, Y. V.; Sullivan, M. J.; Schröder, M.; Yellowlees, L. J. *J. Chem. Soc., Chem. Commun.* **1992**, 848. (x) Setzer, W. N.; Guo, Q.; Grant, G. J.; Hubbard, J. L.; Glass, R. S.; Van der Veer, D. G. *Heteroat. Chem.* **1990**, 317. (y) Bell, M. N.; Blake, A. J.; Holder, A. J.; Hyde, T. I.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1990**, 3841. (z) Rawle, S. C.; Sewell, T. J.; Cooper, S. R. *Inorg. Chem.* **1987**, *26*, 3769. (aa) Rawle, S. C.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1987**, 308. (ab) Bell, M. N.; Blake, A. J.; Kueppers, H. J.; Schröder, M.; Wieghardt, K. *Angew. Chem.* **1987**, *99*, 253.

(7) (a) Shin, R. Y. C.; Bennett, M. A.; Goh, L. Y.; Chen, W.; Hockless, D. C. R.; Leong, W. K.; Mashima, K.; Willis, A. C. *Inorg. Chem.* **2003**, *42*, 96. (b) Goh, L. Y.; Teo, M. E.; Khoo, S. B.; Leong, W. K.; Vittal, J. J. *J. Organomet. Chem.* **2002**, *664*, 161. (c) Shin, R. Y. C.; Teo, M. E.; Leong, W. K.; Vittal, J. J.; Yip, J. H. K.; Goh, L. Y.; Webster, R. D. *Organometallics* **2005**, *24*, 1483. (d) Edwards, A. J.; Willis, A. C.; Wenger, E. *Organometallics* **2002**, *21*, 1654. (e) Eckermann, A. L.; Fenske, D.; Rauchfuss, T. B. *Inorg. Chem.* **2001**, *40*, 1459. (f) Leung, W.-H.; Lau, K.-K.; Zhang, Q.-F.; Wong, W.-T.; Tang, B. *Organometallics* **2000**, *19*, 2084. (g) Grant, G. J.; Salupo-Bryant, T.; Holt, L. A.; Morrissey, D. Y.; Gray, M. J.; Zubkowski, J. D.; Valente, E. J.; Mehne, L. F. *J. Organomet. Chem.* **1999**, *587*, 207. (h) Green, M.; Draganjac, M.; Jiang, Y.; Cordes, A. W. *J. Chem. Crystallogr.* **1999**, *29*, 273. (i) Birri, A.; Steed, J. W.; Tocher, D. A. *J. Organomet. Chem.* **1999**, *575*, 242. (j) Harlow, K. J.; Hill, A. F.; Wilton-Ely, J. D. E. T. *J. Chem. Soc., Dalton Trans.* **1999**, 285. (k) Bennett, M. A.; Willis, A. C.; Goh, L. Y.; Chen, W. *Polyhedron* **1996**, *15*, 3559. (l) Welch, A. J.; Weller, A. S. *Inorg. Chem.* **1996**, *35*, 4548. (m) Bennett, M. A.; Goh, L. Y.; Willis, A. C. *J. Am. Chem. Soc.* **1996**, *118*, 4984. (n) Adams, R. D.; Yamamoto, J. H. *Organometallics* **1995**, *14*, 3704. (o) Adams, R. D.; Falloon, S. B.; McBride, K. T.; Yamamoto, J. H. *Organometallics* **1995**, *14*, 1739. (p) Bennett, M. A.; Goh, L. Y.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1180. (q) Bell, M. N.; Blake, A. J.; Schröder, M.; Stephenson, T. A. *J. Chem. Soc., Chem. Commun* **1986**, 471. (r) Hill, A. F.; Rae, A. D.; Schultz, M.; Willis, A. C. *Organometallics* **2004**, *23*, 81.

(8) For an early review of the coordination chemistry of carbon monosulfide see: Broadhurst, P. V. *Polyhedron* **1985**, *4*, 1801.

(9) CS is not isolable under laboratory conditions but has been spectroscopically observed when CS_2 is subjected to high-frequency electric discharge at −190 °C[10] and in the insterstellar medium.[11],

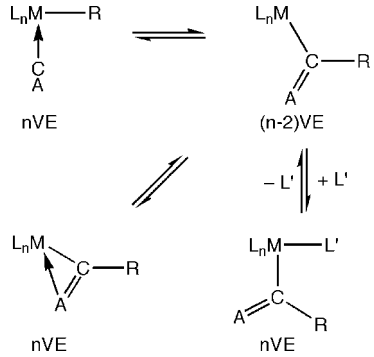
(10) Steudel, R. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 635. (b) Steudel, R. *Z. Naturforsch.* **1966**, *21B*, 1106.

(11) Bull, D. *Sky Telescope* **1973**, 156. (b) Oppenheimer, M.; Delgars, A. *Astrophys. J.* **1974**, *187*, 231. (c) Liszt, H. S.; Links, R. A. *Astrophys. J.* **1975**, *196*, 709.

(12) (a) Saillard, J. Y.; Grandjean, D.; Caillet, P.; Le Beuze, A. J. *Organomet. Chem.* **1980**, *190*, 371. (b) Richards, W. G. *Trans. Faraday Soc.* **1967**, *63*, 257.

(13) (a) Doyle, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 194. (b) Doyle, R. A.; Angelici, R. J. *Organometallics* **1989**, *8*, 2207. (c) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1984**, *3*, 1124. (d) Greaves, W. W.; Angelici, R. J. *Inorg. Chem.* **1981**, *20*, 2983. (e) Greaves, W. W.; Angelici, R. J.; Helland, B. J.; Klima, R.; Jacobson, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7618. (f) Dombek, B. D.; Angelici, R. J. *Inorg. Chem.* **1976**, *15*, 2397. (g) Dombek, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 1261. (h) Desmond, T.; Lalor, F. J.; Ferguson, G.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1984**, 75.

Scheme 1. Valence Electron Counts (*n*VE) Associated with Migratory Insertion (A = O, S)



migrate to CS with ease, including hydrides,[17−21] silyls,[22] boryls,[23] and boranes.[24] Furthermore, CS/alkyne coupling of alkynes, which might be viewed as a special case of migratory insertion, provided the archetypal metallacyclobutadiene[25] and metallabenzenes,[26] the latter being implicated in the formation of cyclopentadiene-thione complexes.[27] Herein we describe the reactions of the recently reported σ-organyl/thiocarbonyl complexes $[Ru(R)Cl(CS)(PPh_3)_2]$ (R = vinyl,[28] aryl[29]) with [9]aneS$_3$, which lead in some but not all cases to migratory insertion. These phenomena have been interpreted with recourse to theoretical methods. Aspects of this work have contributed to a preliminary communication.[4e]

Results and Discussion

The σ-organyl/thiocarbonyl starting complexes for this study are available via two routes. The reaction of $[RuHCl(CS)(PPh_3)_3]$[30] with diphenylmercury provides the coordinatively unsaturated σ-aryl complex $[Ru(C_6H_5)Cl(CS)(PPh_3)_2]$[29] by analogy with that described for the related osmium complex $[Os(C_6H_4Me\text{-}4)Cl(CS)(PPh_3)_2]$.[16a] The series of coordinatively unsaturated σ-vinyl complexes (Scheme 2) arises from the facile hydroruthenation of alkynes by the same hydrido complex,[28] while the 18-electron complex $[Os(CH{=}CHC_6H_4Me)Cl(CS)(BTD)(PPh_3)_2]$ (BTD = 2,1,3-benzothiadiazole),[32b] by virtue of the labile BTD ligand, is synthetically equivalent to a 16-electron species.

Vinyl Complexes. Four representative examples were chosen to illustrate various features: monosubstituted, disubstituted, α-carbomethoxy, and α-alkynyl substituted. The metallacyclic complex $[Ru\{C(CO_2Me){=}CHCO_2Me\}Cl(CS)(PPh_3)_2]$ is coordinatively saturated as a result of the β-ester group; however this coordination appears to be hemilabile. Thus treating the complex with [9]aneS$_3$ in the presence of a salt of a noncoordinating anion (ClO_4^- or PF_6^-) results in the formation of the octahedral vinyl complex $[Ru\{C(CO_2Me){=}CHCO_2Me\}(CS)(PPh_3)([9]aneS_3)]PF_6$ (**1**·PF_6) via opening of the metallacycle and substitution of the chloride and one phosphine ligand (Scheme 3). The facial coordination of the macrocycle follows from the complex ^{1}H NMR data associated with the ligand. In an octahedral complex of the form $[ML^1L^2L^3([9]aneS_3)]$, the chirality at the metal center renders each of the 12 macrocyclic protons chemically distinct. We have in one instance shown that NOESY and COSY techniques allow the identification of each of these resonances;[4a] however detailed analyses were not attempted in the present study. The gross formulation of the cation follows from positive ion FAB-mass spectrometry, which reveals an abundant molecular ion in addition to fragmentations due to loss of vinyl and phosphine ligands. A further feature of complexes of [9]aneS$_3$ is the appearance of fragmentations attributable to ethylene elimination from the macrocycle. A singlet resonance is observed in the $^{31}P\{^1H\}$ NMR spectrum that further confirms tridentate coordination of the macrocycle.

(14) (a) Busetto, L.; Graziani, M.; Belluco, U. *Inorg. Chem.* **1971**, *10*, 78. (b) Brothers, P. J.; Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1980**, *195*, C29. (c) Herberhold, M.; Hill, A. F.; McAuley, N.; Roper, W. R. *J. Organomet. Chem.* **1986**, *310*, 95. (d) Clark, G. R.; Collins, T. J.; Hall, D.; James, S. M.; Roper, W. R. *J. Organomet. Chem.* **1977**, *141*, C5. (e) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1977**, *139*, C9. (f) Singh, M. M.; Angelici, R. J. *Inorg. Chem.* **1984**, *23*, 2691. (g) Singh, M. M.; Angelici, R. J. *Angew. Chem.* **1983**, *95*, 160. (h) Faraone, F.; Piraino, P.; Marsala, V.; Sergi, S. *J. Chem. Soc., Dalton Trans.* **1977**; *Chim. l'Indust.* **1976**, *58*, 654. (i) Wnuk, T. A.; Angelici, R. J. *Inorg. Chem.* **1977**, *16*, 1173.

(15) (a) Dunker, J. W.; Finer, J.; Clardy, J.; Angelici, R. J. *J. Organomet. Chem.* **1976**, *114*, C49. (b) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 5154. (c) Doyle, R. A.; Daniels, L. M.; Angelici, R. J.; Stone, F. G. A. *J. Am. Chem. Soc.* **1989**, *111*, 4995. (d) Dombeck, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 7568. (e) Johnson, A. R.; Davis, W. M.; Cummins, C. C.; Serron, S.; Nolan, S. P.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1998**, *120*, 2071. (f) Jeffrey, J. C.; Razay, H.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1733. (g) Jeffery, J. C.; Razay, H.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1981**, 243. (h) Werner, H.; Kolb, O.; Thometzek, P. *J. Organomet. Chem.* **1988**, *347*, 137. (i) Kolb, O.; Werner, H. *Angew. Chem.* **1982**, *94*, 207. (k) Choi, M. G.; Daniels, L. M.; Angelici, R. J. *J. Organomet. Chem.* **1990**, *383*, 321. (l) Albano, V. G.; Monari, M.; Busetto, L.; Carlucci, L.; Zanotti, V. *Gazz. Chim. Ital.* **1992**, *122*, 201. (m) Busetto, L.; Monari, M.; Palazzi, A.; Albano, V.; Demartin, F. *J. Chem. Soc., Dalton Trans.* **1983**, 1849.

(16) (a) Clark, G. R.; Collins, T. J.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1983**, *259*, 215. (b) Clark, G. R.; Collins, T. J.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1978**, *157*, C23. (c) Rickard, C. E. F.; Roper, W. R.; Woodgate, S. D.; Wright, L. J. J. *Organomet. Chem.* **2001**, *623*, 109. (d) Rickard, C. E. F.; Roper, W. R.; Woodgate, S. D.; Wright, L. J. *J. Organomet. Chem.* **2000**, *607*, 27.

(17) (c) Although migratory coupling of CO and hydrides is on occasion inferred and believed to be kinetically feasible, thermodynamically the hydride-carbonyl tautomer is generally favored over the formyl.[18] An exception is when the formyl may be trapped via formation of a strong metal−oxygen bond[16] or proceed irreversibly via subsequent transformations.[19,20],

(18) Koga, N.; Morokuma, K. *New J. Chem.* **1991**, *15*, 749.

(19) Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959.

(20) (a) Fryzuk, M. D.; Mylvaganam, M.; Zaworotko, M. J.; MacGillivray, L. R. *Organometallics* **1996**, *15*, 1134. (b) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6733. (c) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. J. *Am. Chem. Soc.* **1978**, *100*, 2716. (d) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (e) Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278.

(21) Roper, W. R.; Town, K. G. *J. Chem. Soc., Chem. Commun.* **1977**, 781. (b) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73. (c) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1977**, *139*, C9. (d) Collins, T. J.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1976**, 1044.

(22) (a) Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *Organometallics* **1992**, *11*, 3931. (b) Attar-Bashi, M. T.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J.; Woodgate, S. D. *Organometallics* **1998**, *17*, 504.

(23) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685.

(24) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2007**, *26*, 3891.

(25) Elliot, G. P.; Roper, W. R. *J. Organomet. Chem.* **1983**, *250*, C5.

(26) (a) Elliott, G. P.; Roper, W. R.; Waters, J. M. *Chem. Commun.* **1982**, 811. (b) Clark, G. R.; Johns, P. M.; Roper, W. R.; Wright, L. J. *Organometallics* **2008**, *27*, 451. (c) Clark, G. R.; Johns, P. M.; Roper, W. R.; Wright, L. J. *Organometallics* **2006**, *25*, 1771. (d) Clark, G. R.; Lu, G.-L.; Roper, W. R.; Wright, L. J. *Organometallics* **2007**, *26*, 2167. (e) For a review of metallabenzenes derived from thiocarbonyl ligands see: Wright L. J. *Dalton Trans.* **2006**, 1821.

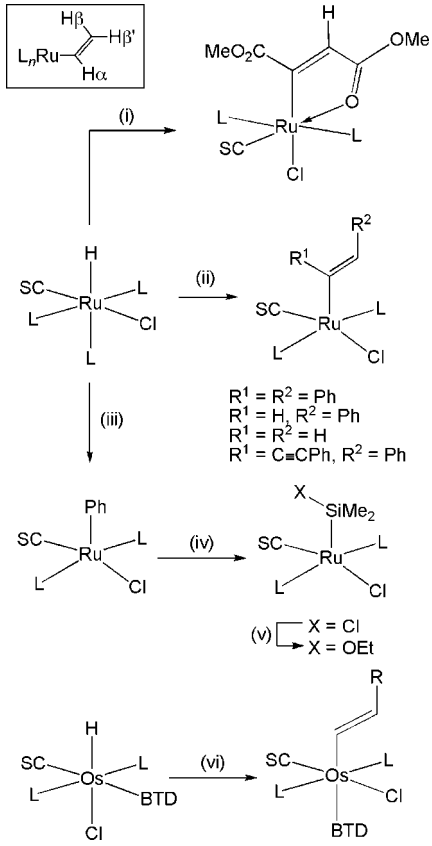
(27) Hill, A. F.; Schultz, M.; Willis, A. C *Organometallics* **2005**, 24–2027.

(28) Cowley, A. R. C.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **2007**, *26*, 6114.

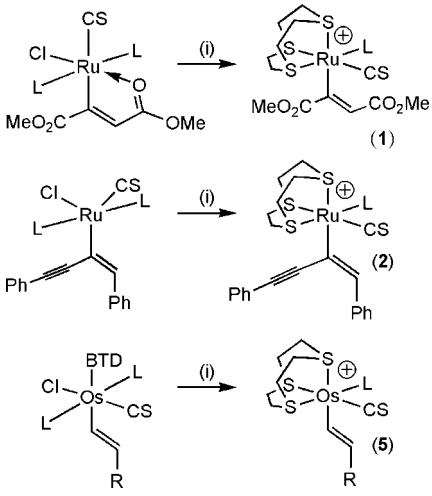
(29) Bedford, R. B.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 95.

(30) Brothers, P. J.; Roper, W. R. *J. Organomet. Chem.* **1983**, *258*, 73.

Scheme 2. Synthesis of Starting Thiocarbonyl Complexes (L = PPh_3): (i) $MeO_2CC{\equiv}CCO_2Me$;[26] (ii) $R^1C{\equiv}CR^2$;[26] (iii) $HgPh_2$;[27] (iv) $SiHClMe_2$;[20] (v) EtOH[20]



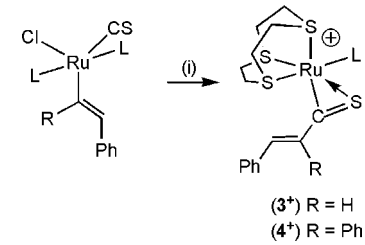
Scheme 3. Reaction of 1,4,7-Trithiacyclononane ([9]$aneS_3$) with Ruthenium and Osmium Thiocarbonyl Alkenyl Complexes (L = PPh_3): (i) [9]$aneS_3$, NH_4PF_6, or $NaClO_4$



Clear evidence that migratory insertion has not ensued is provided by the appearance of an intense absorption at 1290 cm^{-1} due to the terminal thiocarbonyl ligand.

A similar result is obtained for the α-alkynyl-substituted vinyl complex [Ru{C(C≡CPh)=CHPh}Cl(CS)$(PPh_3)_2$], which provides the salt [Ru{C(C≡CPh)=CHPh}(CS)(PPh_3)([9]$aneS_3$)]PF_6 (**2**·PF_6) in high yield (83%). Spectroscopic data for this salt are immediately comparable to those for (**1**·PF_6) and are unremarkable other than to confirm that once again migratory insertion has not occurred (ν_{CS} = 1294 cm^{-1}; $^{13}C_{(CS)}$ = 297.2 (d), J_{CP} = 19.7 Hz). The possibility that the α-alkynyl group

Scheme 4. Reactions of 1,4,7-Trithiacyclononane with Ruthenium Thiocarbonyl Styryl and Stilbenyl Complexes (L = PPh_3): (i) [9]$aneS_3$, $LiClO_4$



(**3**$^+$) R = H
(**4**$^+$) R = Ph

coordinates to the metal center[31] may be ruled out on the basis of both infrared ($\nu_{C\equiv C}$ = 2157 cm^{-1}) and ^{13}C NMR data ($\delta_{C\equiv C}$ = 101.5, 98.6 ppm). The macrocyclic ligand gives rise to four singlet resonances (37.2, 35.2, 34.1, 30.4 ppm), one broadened singlet (34.3 ppm), and a doublet (33.8 ppm, J_{CP} = 5.3 Hz), these latter two resonances arising from the two methylene carbons bound to the sulfur *trans* to the phosphine ligand. The simple vinyl complexes [Ru(CR=CHPh)Cl(CS)$(PPh_3)_2$] (R = H, Ph) both react with [9]$aneS_3$ to provide salts with similar FAB-MS data to the previous examples, confirming the gross composition. The remaining data however indicate that the products involve migratory insertion of the vinyl and thiocarbonyl ligands (Scheme 3), to provide the thioacyl salts [Ru(η^2-SCCR=CHPh)(PPh_3)([9]$aneS_3$)]$^+$ (R = H, **3**·ClO_4; R = Ph, **4**·ClO_4). The bidentate thioacyl (metallathiirene) group is an intense visible chromophore,[14−16] and hence these salts are deep purple. We have so far been unsuccessful in obtaining crystallographic confirmation of the thioacyl formulations; however this follows unambiguously from the following spectroscopic data: Immediate indication that the thiocarbonyl component is no longer terminal in nature follows from the absence of a characteristically intense ν_{CS} absorption in the infrared spectrum of either derivative. In the case of **4**·ClO_4, for which carbon-13 NMR data are available, the thiocarbonyl resonance is observed as a doublet at 312.8 ppm (J_{CP} = 9.7 Hz) in a region typical of metallathiirenes.[11,32] For the thiocinnamoyl example (**3**·ClO_4), only one of the vinylic protons (H_α) was observed in the ^1H NMR spectrum due to the second being obscured by phenyl resonances. This signal, which appears at 7.64 ppm, shows coupling to H_β (11.9 Hz) in addition to a very small coupling (1.7 Hz) to the now more remote (^4J) phosphorus nucleus. The absence of coupling to phosphorus and the change in shift of the Hα resonance to higher field (8.65 ppm, dt, J_{HH} = 14.1, J_{HP} = 2.9 Hz in the alkenyl precursor) indicate that the

(31) (a) Gotzig, J.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247. (b) Jia, G.; Rheingold, A. L.; Meek, D. W. *Organometallics* **1989**, *8*, 1378. (c) Jia, G.; Gallucci, J. C.; Rheningold, A. L.; Haggerty, B. S.; Meek, D. W. *Organometallics* **1991**, *10*, 3459. (d) Jia, G.; Meek, D. W. *Organometallics* **1991**, *10*, 1444. (e) Field, L. D.; George, A. V.; Hambley, T. W. *Inorg. Chem.* **1990**, *29*, 4565. (f) McKullen, A. K.; Selegue, J. P.; Wang, J.-G. *Organometallics* **1991**, *10*, 3421. (g) Bianchini, C.; Peruzzini, M.; Zanobini, F.; Frediani, P.; Albinati, A. *J. Am. Chem. Soc.* **1991**, *113*, 5453. (h) Alcock, N. W.; Hill, A. F.; Melling, R. P.; Thompsett, A. R. *Organometallics* **1993**, *12*, 641. (i) Hill, A. F.; Melling, R. P.; Thompsett, A. R. *J. Organomet. Chem.* **1991**, *402*, C8. (j) Hill, A. F.; Melling, R. P. *J. Organomet. Chem.* **1990**, *396*, C22.

(32) (a) Anderson, S.; Cook, D. J.; Hill, A. F. *Organometallics* **2001**, *20*, 2468. (b) Hill, A. F.; Wilton-Ely, J. D. E. T. *J. Chem. Soc., Dalton Trans.* **1998**, 3501. (c) Andon, W.; Ohtaki, T.; Suzuki, T.; Kabe, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7782. (d) Drews, R.; Edelmann, F.; Behrens, U. *J. Organomet. Chem.* **1986**, *315*, 369. (e) Faraone, F.; Tresoldi, G.; Loprete, G. A. *J. Chem. Soc., Dalton Trans.* **1979**, 933. (f) Tresoldi, G.; Faraone, F.; Piraino, P. *J. Chem. Soc., Dalton Trans.* **1979**, 1053. (g) Hill, A. F.; Malget, J. M. *J. Chem. Soc., Dalton Trans.* **1997**, 2003. (h) Cook, D. J.; Hill, A. F. *Organometallics* **2003**, *22*, 3502. (i) Cook, D. J.; Hill, A. F. *J. Chem. Soc., Chem. Commun.* **1997**, 955.

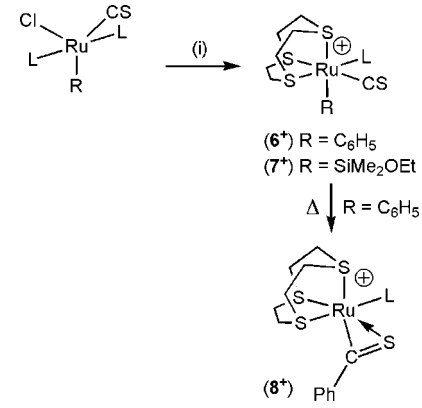
CH═CHPh moiety is no longer directly bonded to the ruthenium center. We have also reported the preparation of the osmium species $[Os(CH{=}CHC_6H_4Me\text{-}4)Cl(CS)(BTD)(PPh_3)_2]$, which reacts with carbon monoxide to yield the thioacyl complex $[Os(\eta^2\text{-}SCCH{=}CHC_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$.[32b] However, treatment of $[Os(CH{=}CHC_6H_4Me\text{-}4)Cl(CS)(BTD)(PPh_3)_2]$ with [9]aneS$_3$ in the presence of NH_4PF_6 provides the nonmigrated product $[Os(CH{=}CHC_6H_4Me\text{-}4)(CS)(PPh_3)([9]aneS_3)]PF_6$ (**5**·PF$_6$) in 69% yield. This complex gives rise to an intense ν_{CS} absorption at 1298 cm^{-1}, and the remainder of the data compare well with those of the carbonyl analogue $[Os(CH{=}CHC_6H_4Me\text{-}4)(CO)(PPh_3)([9]aneS_3)]PF_6$.[32b]

Aryl and Silyl Complexes. Given that the vinyl complexes discussed above led to different products upon reaction with [9]aneS$_3$, we have briefly investigated the reactions of the complexes $[Ru(C_6H_5)Cl(CS)(PPh_3)_2]$[29] and $[Ru(SiMe_2OEt)Cl(CS)(PPh_3)_2]$[22] with [9]aneS$_3$. While both of these species react with carbon monoxide to provide thioacyl complexes, the latter example described by Roper[22] is remarkable in that silyl groups are characteristically not prone to such processes. With the exception of early transition metal (d^0) sila-acyl complexes reported by Tilley that result from the carbonylation of the corresponding silyl complexes,[33] sila-acyls are in general only accessible via *external* nucleophilic attack by silyl anions on coordinated CO,[34,35] typically as intermediates en route to silylcarbenes and carbynes.[35] Thus the high propensity of thiocarbonyl ligands for migratory insertion processes is emphatically illustrated, though the formation of a Ru−S bond in adopting the bidentate coordination mode no doubt contributes to the thermodynamic impetus.

Treating both $[Ru(C_6H_5)Cl(CS)(PPh_3)_2]$ and $[Ru(SiMe_2OEt)Cl(CS)(PPh_3)_2]$ with [9]aneS$_3$ leads to tridentate coordination of the macrocycle, as for the vinyl complexes above; however there is no indication of migratory insertion of either the phenyl or silyl ligands with the thiocarbonyl under ambient conditions. Thus the salts $[Ru(C_6H_5)(CS)(PPh_3)([9]aneS_3)]PF_6$ (**6**·PF$_6$) and $[Ru(SiMe_2OEt)(CS)(PPh_3)([9]aneS_3)]PF_6$ (**7**·PF$_6$) are readily obtained in 72% and 83% yield, respectively (Scheme 5). The formulations follow unambiguously from spectroscopic data. The presence of intense infrared absorptions at 1293 (R = Ph) and 1275 cm^{-1} (R = SiMe$_2$OEt) confirms that the terminal thiocarbonyl retains its integrity in both products. However, on heating in tetrahydrofuran for 4 h, **6**·PF$_6$ was found to convert smoothly into the thiotoluoyl complex $[Ru(\eta^2\text{-}SCC_6H_5)(PPh_3)([9]aneS_3)]PF_6$ (**8**·PF$_6$), which displays no terminal thiocarbonyl absorption. The products **6**·PF$_6$ and **8**·PF$_6$ give similar FAB-MS spectra and microanalytical data, indicating an identical empirical composition but differ in ^{1}H and ^{31}P NMR chemical shift (39.4 ppm for **6**·PF$_6$ and 35.9 ppm for **8**·PF$_6$) and the presence of a coordinated terminal ν_{CS} absorption. The data for **8**·PF$_6$ associated with the SCR ligand also compare well to those for $[Ru(\eta^2\text{-}SCC_6H_5)(CA)(PPh_3)_2]$ (A = O, S).[29]

The nature of [9]aneS$_3$ bonding to a metal is a matter for debate[2] in that while phosphines PR$_3$ are often supposed to involve a variable degree of retrodonation into π-acidic P(d) or P−R (σ^*) orbitals, such interactions for thioethers are less clear-cut. In general macrocycle C−S bonds become elongated in metal complexes relative to free [9]aneS$_3$, and calculations indicate that for the complexes $[M([9]aneS_3)_2]^{n+}$ (M^n = Tc^1, Ru^{II}, Rh^{III}) there is considerable population of C−S σ^* orbitals.[36] A π-acidic component to the bonding of [9]aneS$_3$ complexes would certainly be in concert with the observed ability of this ligand to induce migratory insertion, given that migratory insertion is generally favored by any factor that reduces retrodonation to the (thio)carbonyl ligand. We have addressed this qualitative interpretation in two ways. Experimentally, we have investigated the reactions of the model σ-organyl/thiocarbonyl precursors with sulfur chelates that have π-basic character in the expectation that migratory insertion would not be favored. Second (*vide infra*) we have computationally interrogated the electronic nature of species on the migratory insertion reaction coordinate.

Scheme 5. Reaction of 1,4,7-Trithiacyclononane with Ruthenium Aryl and Silyl Compounds (L = PPh$_3$): (i) [9]aneS$_3$, NH$_4$PF$_6$; (ii) heat (R = Ph only)



Reactions with π-Basic Sulfur Chelates. In contrast to [9]aneS$_3$ which is primarily a σ-donor ligand with at best a modest degree of π-acidity,[36] dithiocarbamates are strongly π-basic.[37] The reaction of $[Ru(CH{=}CHPh)Cl(CS)(PPh_3)_2]$ with $Na[S_2CNMe_2]$ was investigated and found to provide the noninserted vinyl complex $[Ru(CH{=}CHPh)(S_2CNMe_2)(CS)(PPh_3)_2]$ (**9**), as indicated by the appearance of an intense thiocarbonyl absorption (Nujol: 1251 cm^{-1}) and also by the double-triplet multiplicity of the low-field ^{1}H NMR resonance (δ_H = 8.00 ppm, dt, J_{HH} = 17.2, J_{HP} = 2.3 Hz) due to the α-proton of the vinyl group that remains bound to ruthenium (Scheme 6).

In a similar manner, the reaction of $[Ru(CH{=}CH_2)Cl(CS)(PPh_3)_2]$ with tricyclohexylphosphonio dithiocarboxylate (Cy_3PCS_2) was investigated and found, in the presence of $NH_4[PF_6]$, to provide the salt $[Ru(CH{=}CH_2)(S_2CPCy_3)(CS)(PPh_3)_2]PF_6$ (**10**·PF$_6$). We have previously described the analogous carbonyl salt $[Ru(CH{=}CHC_6H_4Me\text{-}4)(S_2CPCy_3)(CO)(PPh_3)_2]Cl$ and also noted that the hydride-thiocarbonyl complex $[RuHCl(CS)(PPh_3)_3]$ is not converted to a thioformyl derivative by Cy_3PCS_2, but rather provides the complex $[RuH(S_2CPCy_3)(CS)(PPh_3)_2]Cl$, while $[RuHCl(CO)(PPh_3)_3]$ provides a mixture of the two complexes $[RuH(S_2CPCy_3)(CO)(PPh_3)_2]^+$ and $[Ru(S_2CHPCy_3)(CO)(PPh_3)_2]^+$.[38]

(33) (a) Camion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049. (b) Woo, H.-G.; Freeman, W. P.; Tilley, T. D. *Organometallics* **1992**, *11*, 2198.

(34) Anglin, J. R.; Calhoun, H. P.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 2281.

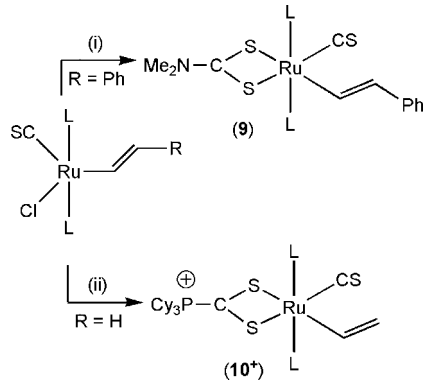
(35) (a) Fischer, E. O.; Hollfelder, H.; Friedrich, P.; Kreibl, F. R.; Huttner, G. *Angew. Chem., Int. Ed.* **1977**, *16*, 401. (b) Jamison, G. M.; Bruce, A. E.; White, P. S.; Templeton, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 5057. (c) Jeffery, J. C.; Ruiz, M. A.; Stone, F. G. A. *J. Organomet. Chem.* **1988**, *355*, 231. (d) Wadepohl, H.; Arnold, U.; Pritzkow, H.; Calhorda, M. J.; Veiros, L. F. *J. Organomet. Chem.* **1999**, *587*, 233.

(36) Mullen, G. E. D.; Fassler, T. F.; Went, M. J.; Howland, K.; Stein, B.; Blower, P. J. *J. Chem. Soc., Dalton Trans.* **1999**, 3759.

(37) For a recent comprehensive review of dithiocarbamate coordination chemistry see: Hogarth, G. *Prog. Inorg. Chem.* **2005**, *53*, 71.

(38) Hector, A. L.; Hill, A. F. *J. Organomet. Chem.* **1993**, *447*, C7.

Scheme 6. Reactions of Vinyl-thiocarbonyl Complexes with π-Basic Chelates (L = PPh_3): (i) $Na[S_2CNMe_2]$; (ii) Cy_3PCS_2, $[NH_4]PF_6$



Scheme 7. Reaction Pathway for Migratory Insertion (L = PPh_3, for R see Tables 1 and 2)

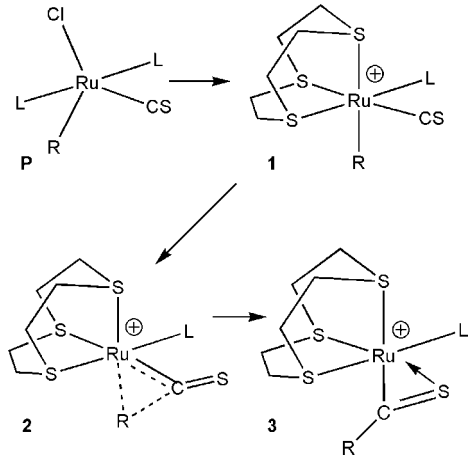


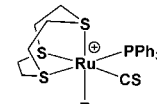
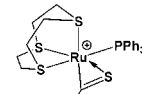
Table 1. Experimental Reactivity of an Array of Ligands Towards Migratory Insertion with Coordinated CS

	R	reactive conditions
a	CH=CHPh	rt
b	CPh=CHPh	rt
c	Ph	reflux in THF (339 K), 4 h
d	C(C≡CPh)=CHPh	unreactive at rt; reflux untried
e	$C(CO_2Me)$=$CHCO_2Me$	unreactive at rt; reflux untried
f	$SiMe_2OEt$	unreactive upon reflux in THF

Thus, neither dithiocarbamate nor phosphonio dithiocarboxylate ligands induce migratory insertive coupling of vinyl and thiocarbonyl ligands, consistent with the above arguments that π-donor ligands disfavor such processes.

Computational Studies. The variation in propensity of the migratory insertion reactions for vinyl, aryl, and silyl ligands with coordinated CS described above and summarized in Table 1 calls for more insight, which we expected might follow from computational studies. The key points of interest along the reaction coordinate (Scheme 7) are the 16-electron precursors (**Pa**−**f**), which with [9]aneS_3 convert to the pseudo-octahedral cationic "half-sandwich" complexes **1** (isolable for R = Ph, C(C≡CPh)=CHPh, $C(CO_2Me)$=$CHCO_2Me$, $SiMe_2OEt$), which in *some but not all cases* either spontaneously (R = CH=CHPh, CPh=CHPh) or with heating (R = Ph) evolve to the thioacyls **3** presumably via a three-center-two-electron bonded reactive intermediate **2**. Thus at room temperature, [9]aneS_3 displaces chloride and a phosphine from precursors $[Ru(R)Cl(CS)(PPh_3)_2]$ (**Pa**−**f**) to yield **3a**,**b** and **1c**−**f**. Upon reflux in THF (bp = 66 °C), **1c** presumably rearranges via **2c** to **3c**. Heating under reflux

Table 2. Migrated and Nonmigrated [9]aneS_3 (*not observed)

R		
CH=CHPh	**1a***	**3a**
CPh=CHPh	**1b***	**3b**
Ph	**1c**	**3c**
C(CαCPh)=CHPh	**1d**	**3d***
$C(CO_2Me)$=$CHCO_2Me$	**1e**	**3e***
$SiMe_2OEt$	**1f**	**3f***

in THF of **1f** does not yield **3f**. By modeling **2**, **2TS** (the transition state between **1** and **2**) and **3**, several questions may be answered: Can formation of **3a**,**b** occur stepwise through **1a**,**b** at room temperature? Why does **1c** need heat to react? Why does **1f** not react further on heating, and why do **1d**,**e** not proceed to **3d**,**e** at room temperature and will heat induce reaction?

The Gibbs' free energy of **1TS** relative to **1** can be interpreted as the reaction barrier (Figure 1). **1TSa**,**b** are only +62.52 and +60.64 kJ/mol relative to their respective reactants, and reaction is expected to occur easily. **1TSc**−**e** give reasonable reaction barriers (95.17, 84.12, and 101.24 kJ/mol) for a heated reaction. (Note: alternative structures for **1TSd** with the alkynyl moiety *syn* to the phosphine are precluded by the cone angle of PPh_3, and another alternative with the phenyl rings in-plane with each other results in a higher barrier). Systems **a**−**e** are exergonic, and equilibrium favors formation of product if the reaction barrier is surmountable. **1TSa**−**e** structures (Figure 2) match well with previously reported transition states for CO insertion

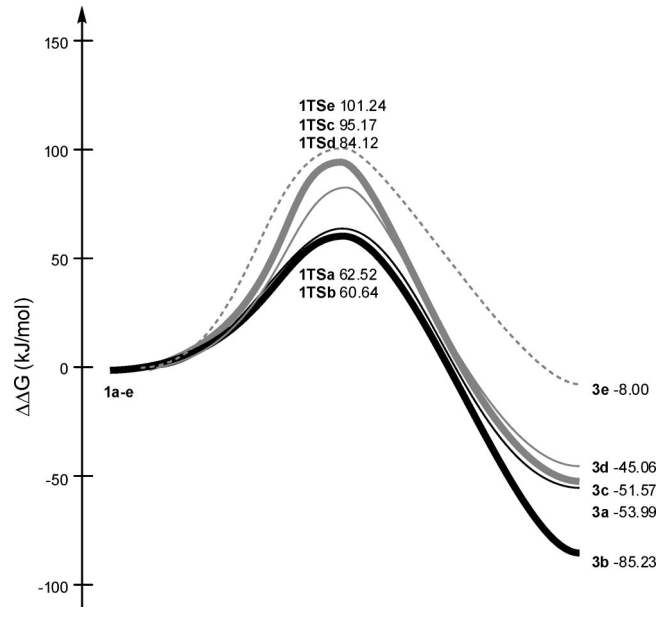


Figure 1. Relative reaction profiles for systems **a**−**e**. Intermediates **2a**−**e** are not shown for clarity, and ensuing transition states toward **3a**−**e**, while not found, are not expected to affect the overall reaction barrier.

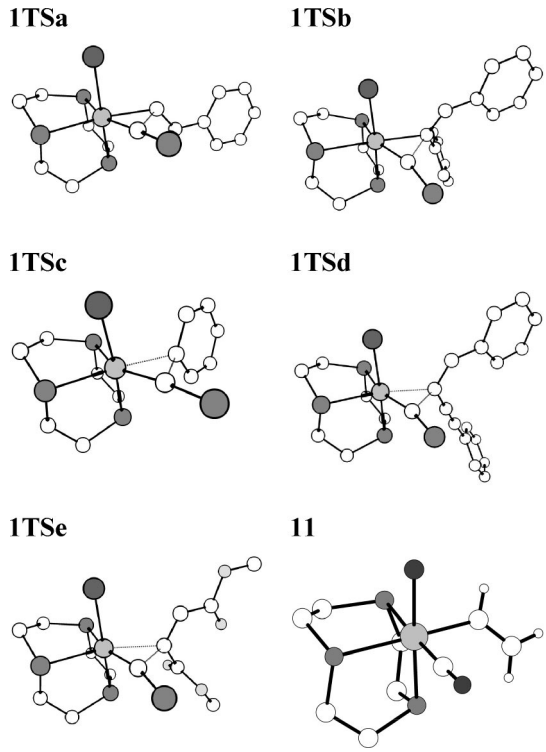


Figure 2. Transition states **1TSa**−**e** and the ground-state geometry for $[Ru(CH{=}CH_2)(CO)(PPh_3)([9]aneS_3)]^+$ (**11**, taken from ref 4a. Hydrogens have been omitted for clarity.

into Co−vinyl bonds; the π-system of the group R is aligned with the newly forming C−C bond.[39]

The overall reaction **1f** to **3f** is endergonic ($\Delta G = +32.98$ kJmol^{-1}). This difference from the other systems can be rationalized as being due to the weakness of the Si−C bond and the lack of π-conjugation in the product. Even if the reaction barrier were very low (unlikely, given the presumed five-coordinate nature of silicon at **1TSf**), thermodynamics would prohibit a significant yield of **3f**. Thus, no attempt was made to find **1TSf** or **2f**.

Previous carbonylation studies have observed that electron-withdrawing (EW) substituents on the migrating ligand inhibit reaction or that electron-donating (ED) ones promote it.[8−11] Such trends are difficult to observe in **a**−**e** because of the widely varying steric profiles of the ligands. To determine the electronic effect of substituents on thiocarbonyl insertion, a series of hypothetical systems **g**−**k** and **m**, employing sterically consistent, *para*-substituted phenyls, have been modeled and compared with **c** (Table 3). Indeed, EW substituents do increase ΔE_{1TS}, inhibiting reaction. Does this effect stem from stabilization of **1** or from destabilization of **1TS**? To find out, the structures are partitioned into ligand and metal fragments. Single-point calculations are run on the fragments of systems **c** and **g**−**j**. By comparing the energies of the sum of the fragments versus the energy of the whole system, ligand binding energies (LBEs) may be determined (Scheme 8).

Surprisingly, it is found that EW substituents correlate with *weaker* bonding in **1** (Table 3). The electrostatic contribution

Table 3. Substituent Effects on Ligand Binding Energy of Reactant and Relative SCF Energy of Transition State and Product

	R	LBE1 (kJ mol^{-1})	ΔE_{1TS} (kJ mol^{-1})	ΔE_3 (kJ mol^{-1})
g	*p*-$NH_2C_6H_4$	−385.53	69.27	−87.19
h	*p*-OHC_6H_4	−376.77	79.14	−72.51
i	*p*-$CH_3C_6H_4$	−374.78	92.25	−62.14
c	Ph	−371.51	93.58	−55.33
j	*p*-FC_6H_4	−372.87	95.26	−59.14
k	*p*-$CHOC_6H_4$	−366.91	97.64	−47.76
m	*p*-$NO_2C_6H_4$	−366.75	102.96	−41.24

Scheme 8. Ligand Binding Energy (fragment charges are consistent with homolytic cleavage of the Ru−R bond)

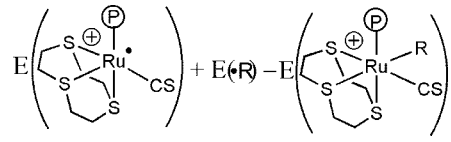


Table 4. Frontier Symmetry-Adapted Fragment Orbital Gross Populations[a]

	ligand HO−2	ligand HO−1	ligand HOFO	ligand LUFO	metal HO−1	metal HOFO	metal LUFO	metal LU+1
1g	1.99	1.20	**1.94**	0.00	1.96	0.80	0.02	0.01
1TSg	1.99	**1.78**	1.22	0.01	1.99	0.98	0.05	0.07
3g	2.00	1.68	0.90	0.00	1.98	1.38	0.31	0.02
1h	1.99	**1.96**	1.20	0.01	1.96	0.79	0.01	0.01
1TSh	1.99	1.82	1.21	0.01	2.00	0.99	0.05	0.07
3h	2.00	**1.74**	0.92	0.00	1.98	1.37	0.26	0.02
1i	1.99	1.96	1.20	0.01	1.96	0.79	0.01	0.01
1TSi	1.99	1.81	1.16	0.02	1.97	1.10	0.04	0.08
3i	2.00	**1.76**	0.93	0.01	1.98	1.38	0.23	0.02
1c	1.99	**1.97**	1.21	0.01	1.96	0.78	0.01	0.01
1TSc	1.99	**1.84**	1.18	0.01	1.99	1.05	0.04	0.06
3c	2.00	**1.78**	0.93	0.00	1.98	1.37	0.21	0.02
1j	1.99	**1.97**	1.22	0.01	1.96	0.77	0.01	0.01
1TSj	1.99	**1.82**	1.17	0.01	1.98	1.08	0.04	0.07
3j	2.00	**1.77**	0.92	0.00	1.98	1.37	0.23	0.01
1k	1.97	2.00	1.23	0.03	1.96	0.76	0.01	0.01
1TSk	1.85	2.00	1.17	0.05	1.99	1.07	0.05	0.06
3k	1.82	2.00	0.93	0.03	1.98	1.36	0.19	0.02
1m	1.99	2.00	1.24	0.02	1.96	0.74	0.01	0.01
1TSm	1.86	2.00	1.18	0.04	1.99	1.05	0.04	0.05
3m	1.82	2.00	0.93	0.02	1.98	1.35	0.17	0.02
1a	2.00	**1.96**	1.19	0.03	1.95	0.80	0.01	0.01
1TSa	2.00	**1.76**	1.21	0.07	1.99	0.95	0.09	0.07
3a	2.00	**1.70**	0.94	0.05	1.98	1.37	0.29	0.01
1b	2.00	**1.94**	1.30	0.03	1.97	0.77	0.01	0.01
1TSb	2.00	**1.73**	1.34	0.07	1.99	0.97	0.02	0.14
3b	2.00	**1.67**	1.05	0.06	1.97	1.36	0.29	0.02
1d	2.00	**1.97**	1.31	0.02	1.96	0.74	0.01	0.01
1TSd	2.00	**1.79**	1.30	0.05	1.99	0.94	0.07	0.09
3d	1.99	**1.78**	1.05	0.03	1.97	1.35	0.28	0.01
1e	1.94	**1.96**	1.41	0.05	1.94	0.67	0.00	0.01
1TSe	1.94	**1.93**	1.33	0.09	1.99	0.98	0.07	0.06
3e	1.90	**1.91**	1.12	0.06	1.97	1.31	0.13	0.04

[a] HOFO and LUFO stand for "highest occupied fragment orbital" and "lowest unoccupied fragment orbital", respectively. Bold entries denote the highest occupied π orbital of the ligand fragment.

to bonding favors a negative charge on the α-carbon (next to the positively charged metal), which EW substituents inhibit. Further, gross populations of the symmetry-adapted fragment orbitals (SFOs) reveal that π-back-bonding is minimal, presumably due to the formal +1 charge of the ruthenium, the competitively π-acidic thiocarbonyl ligand, and the low-symmetry environment (Table 4). This result discounts the possibility that EW-substituted ligands are inert due to a greater M−R bond strength. Instead, the inhibitory effect of EW substituents lies in **1TS**. The difference in Hirshfeld charge[44] between the metal fragment and the ligand decreases by 0.39−0.45 going from **1** to **1TS**. Approximately 0.2 electron is transferred from the ligand to the metal fragment (Table 5).

(39) Luo, X. L.; Tang, D. Y.; Ming, L. *J. Mol. Struct.* **2006**, *765*, 21.
(40) Markies, B. A.; Wijkens, P.; Dedieu, A.; Boersma, J.; Spek, A. L.; Van Koten, G. *Organometallics* **1995**, *14*, 5628–5641.
(41) Bassetti, M.; Sunley, G. J.; Fanizzi, F. P.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1990**, 1799.
(42) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1986**, *108*, 6136.
(43) Sugita, N.; Minkiewicz, J. V.; Heck, R. F. *Inorg. Chem.* **1978**, *17*, 2809.

Table 5. Changes in Hirshfeld Charge Differences between Metal and Ligand Fragments from 1 to 1TS and 1 to 3

	system										
	g	**h**	**i**	**c**	**j**	**k**	**m**	**a**	**b**	**d**	**e**
ΔΔHirshfeld charge$_{1TS}$	−0.39	−0.40	−0.45	−0.39	−0.44	−0.43	−0.41	−0.43	−0.41	−0.42	−0.45
ΔΔHirshfeld charge$_{3}$	−0.88	−0.80	−0.75	−0.72	−0.76	−0.72	−0.71	−0.80	−0.69	−0.88	−0.81

According to the SFO populations (Table 4), charge transfer occurs primarily from the highest occupied π orbital (HOPO) of the ligand to the metal fragment's singly occupied fragment orbital (SOFO). This occurs less readily with EW substituents and more easily with ED substituents. As the energy of the SOFO of the metal fragment does not vary much between systems, the energy of the ligand HOPO inversely correlates with reaction barrier (Figure 3).

In **3**, SFO population analysis shows significant π-donation from the aryl substituent to the CS unit, evidenced by the partial population of the thioacyl fragment orbitals. Also, the ligand SOMO, previously forming a polar Ru−R σ-bond, loses electron density in forming a more covalent SC−R σ-bond. This explains why reaction with ED-substituted ligands is more exothermic than with EW-substituted ligands (and allows **j**, containing a π-donating, σ-withdrawing fluoride substituent, to be slightly more exothermic than **c**). Conversely, the reverse migration reaction faces a smaller barrier with EW-substituted ligands. This agrees with previously reported electronic substituent effects in decarbonylation reactions.[45] An elegant demonstration of this was provided by Roper and Wright[46]and involves the σ-aryl complexes shown in Scheme 9. In solution, the 4-tolyl derivative is in equilibrium with the corresponding benzoyl isomer, though the former is favored; The 4-nitrophenyl complex exists entirely in the σ-aryl-dicarbonyl form, while reduction to the 4-amino derivative results in exclusive formation of the benzoyl isomer. However protonation of the amino groups, which removes its π-donor capacity, results in migration of the aryl ligand back to ruthenium. It was previously inferred that the electron-donating nature of the 4-amino substituent weakened the Ru−C bond of the σ-aryl isomer, thereby favoring migratory insertion. The above results however would suggest that it is stabilization of the electrophilic benzoyl carbon that is the more determining factor.

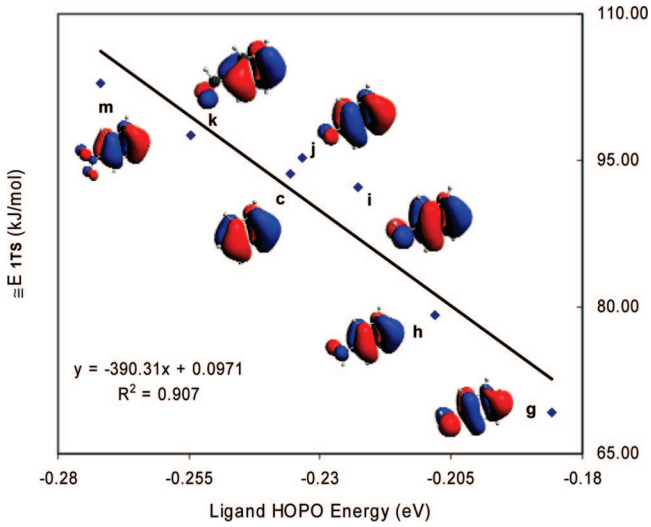


Figure 3. Energy of highest occupied π orbitals of ligand fragments plotted against relative SCF energy of their respective transition states **1TS**(**c**,**g**−**k**,**m**).

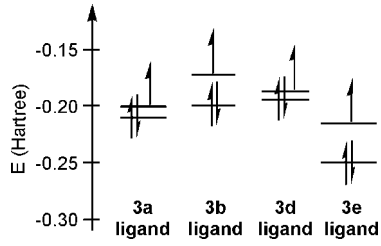


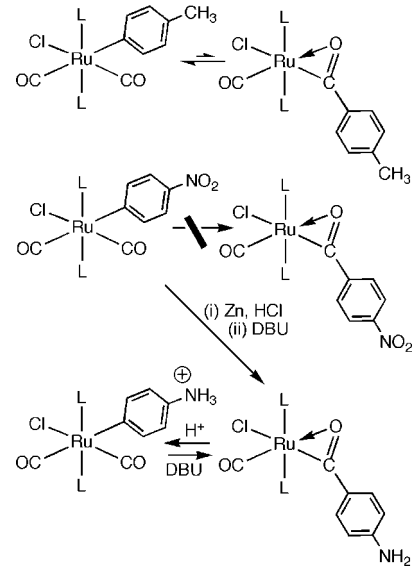
Figure 4. Highest occupied π orbitals and singly occupied orbitals of substituted vinyl ligand fragments of **3a**,**b**,**d**,**e**.

The inverse correlation between HOPO energy and reaction barrier does not cleanly apply to the substituted vinyl systems **a**,**b**,**d**,**e** due to varying steric effects and (in **b**,**d**,**e**) the presence of multiple high-lying π orbitals. However, because steric forces vary less among **3a**,**b**,**d**,**e** than in **1TSa**,**b**,**d**,**e**, the net thermodynamic driving force can still be rationalized as the result of the electron-donating ability of the ligands. Again, SFO population analysis finds that most of the electron donation occurs from the HOPO and SOFO of the ligand fragments. **3b** has the highest ligand SOFO and is the most thermodynamically favorable product. **3a**, due to the low steric profile of the ligand, is able to form a shorter SC−R bond to compensate for its relatively low-lying HOPO and SOFO. **3d** is correctly more favorable than **3e**, which has the lowest-lying HOPO and SOFO of all (Figure 4).

Concluding Remarks

It could be argued that the results described herein do not necessarily translate *in toto* to the more general manifold of migratory insertion. Nevertheless, we have tried both experimentally and computationally to separate the variables that are contributing factors, and some of these inferences will be more generally applicable. First, the computational studies indicate that while the π-basicity of the migrating group may in some part contribute to a destabilization of the ground-state precursor through a compromise in the covalent versus ionic character of

Scheme 9. Effect of *p*-Substituents upon Migratory Insertion of σ-Aryl Ligands (L = PPh$_3$)[46]



the metal−carbon bond, it is the mesomeric stabilization of the resulting thioacyl ("metallathiirene") product that appears to dominate the energetics. This interpretation is of course biased by the cationic nature of both precursors and products, and perhaps by the possible π-acid role of the [9]aneS_3 ligand, to which we have previously alluded. For this reason the reactions of suitable precursors with π-basic sulfur chelates were investigated, including one example that generates a cationic product that *does not* enter into migratory insertion (Cy_3PCS_2).

In the present system, vinyl ligands appear more prone to migratory insertion than simple aryls (or silyls), and this result is consistent with the general observations of Maitlis.[47] We have previously shown that vinyl ligands are capable of irreversibly migrating onto a transient methylene ligand[48] following Roper's illustration that aryl groups in analogous complexes preferentially, albeit reversibly, migrate to an adjacent carbonyl.[49] Within the series of vinyl compounds investigated herein it however becomes apparent that the presence of an electron-withdrawing substituent (CO_2Me or C≡CPh) on the α-carbon of the vinyl group disfavors migration, presumably by enhancing the metal−vinyl bond strength, but also by reducing the mesomeric stabilization of the resulting metallathiirene.

Experimental Section

General Procedures. All operations were carried out under aerobic conditions. All solvents were used as received. Multinuclear NMR spectra were recorded in $CDCl_3$ (unless otherwise stated) at 25 °C on a Jeol JNM EX270 NMR spectrometer. Infrared spectra were recorded as both dichloromethane solutions and Nujol mulls using Perkin-Elmer 1720-X or Mattson Series 1 FT-IR spectrometers. Characteristic "fingerprint" bands for PPh_3 are omitted. FAB-mass spectrometry was carried out using an Autospec Q instrument with 3-nitrobenzyl alcohol (nba) as a matrix. The elimination of ethylene was a recurrent feature in the mass spectra, as has been noted previously for complexes of [9]aneS_3.[36] Quoted yields take into account dichloromethane, which was in the majority of cases found (^{1}H NMR) to form solvates with salts. Elemental analysis was carried out by the Imperial College Microanalytical Service and SACS at London Metropolitan University. In the case of analytical data for partial solvates, the stoichiometry was confirmed, where possible, by ^{1}H NMR integration. The compounds $[Ru(C_6H_5)Cl(CS)(PPh_3)_2]$,[29] $[Ru(SiMe_2OEt)Cl(CS)(PPh_3)_2]$,[22] $[Ru(CR{=}CHPh)Cl(CS)(PPh_3)_2]$ (R = H, Ph, C≡CPh), $[Ru(CH{=}CH_2)Cl(CS)(PPh_3)_2]$, $[Ru\{\kappa^2\text{-}C(CO_2Me){=}CHCO_2Me\}Cl(CS)(PPh_3)_2]$,[28] and $[Os(CH{=}CHC_6H_4Me\text{-}4)Cl(CS)(BTD)(PPh_3)_2]$[32b] were prepared as described elsewhere. All other reagents were used as received from commercial sources. NB: CAUTION although no problems were encountered, perchlorate salts should be treated with care due to the risk of spontaneous detonation.

Preparation of [Ru{C(CO$_2$Me)=CHCO$_2$Me}(CS)(PPh$_3$)([9]aneS$_3$)]PF$_6$ (1·PF$_6$). $[Ru\{\kappa^2\text{-}C(CO_2Me){=}CHCO_2Me\}Cl(CS)(PPh_3)_2]$ (200 mg, 0.236 mmol) and 1,4,7-trithiacyclononane (50 mg, 0.277 mmol) were dissolved in dichloromethane (40 mL). This solution was then treated with NH_4PF_6 (110 mg, 0.675 mmol) in a mixture of water (20 mL) and ethanol (40 mL) and the mixture stirred overnight. Ethanol (40 mL) was added and the volume reduced until crystallization was complete. The resulting yellow crystals were washed with petroleum ether (20 mL) and dried under vacuum. The spectroscopically pure crude product can be recrystallized from dichloromethane and ethanol. Yield: 180 mg (87%). IR (CH_2Cl_2): 1710 $\nu_{C=O}$, 1567 $\nu_{C=O}$ or $\nu_{C=C}$ cm^{-1}. IR (Nujol): 1722, 1713 $\nu_{C=O}$, 1567 $\nu_{C=O}$, 1331, 1290 ν_{CS}, 1204, 1155, 947, 907, 855, 852, 833, 820 cm^{-1}. NMR ^{1}H: δ 2.09, 2.27, 2.83, 3.10 − 3.35, 3.36 (m × 5, 12 H, CH_2), 3.52, 3.79 (s × 2, 3 H × 2, OCH_3), 5.28 (s, 1 H, *C*=CH), 7.30−7.85 (m, 15 H, C_6H_5). ^{31}P{^{1}H}: δ 37.2 ppm. FAB-MS *m*/*z* (% abundance): 731 (100) $[M]^+$, 702 (3) $[M - C_2H_4]^+$, 469 (6) $[M - PPh_3]^+$, 441 (18) $[M - C_2H_4 - PPh_3]^+$, 407 (6) $[M - C(CO_2Me){=}CHCO_2Me - [9]aneS_3]^+$. Microanalytical data were obtained for the corresponding and more crystalline perchlorate salt (1·ClO_4)·$2CH_2Cl_2$ prepared in an identical manner ($LiClO_4$ in place of NH_4PF_6). Spectroscopic data associated with the cation are however identical to those for 1·PF_6. Anal. Found: C, 43.6; H, 3.9. Calcd for $C_{28}H_{34}ClO_8PRuS_4 \cdot 2CH_2Cl_2$: C, 43.3; H, 4.0. Dichloromethane of solvation confirmed by ^{1}H NMR integration.

Preparation of [Ru{C(C≡CPh)=CHPh}(CS)(PPh$_3$)([9]aneS$_3$)]PF$_6$ (2·PF$_6$). A solution of $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CS)(PPh_3)_2]$ (270 mg, 0.297 mmol) in dichloromethane (30 mL) and ethanol (10 mL) was treated with [9]aneS_3 (60 mg, 0.333 mmol) and a solution of KPF_6 (110 mg, 0.598 mmol) in water (1 mL) and ethanol (10 mL) and then stirred for 30 h. All solvent was then removed and the crude product dissolved in dichloromethane and filtered through diatomaceous earth to remove KCl. Ethanol was then added, and crystals were obtained by slow rotary evaporation. The off-white product was filtered off, washed with ethanol (10 mL) and petroleum ether (10 mL), and dried under vacuum. Yield: 230 mg (83%). IR (Nujol): 2157 ν_{CC}, 1977, 1715, 1593, 1581, 1572, 1294 ν_{CS}, 904, 840 (PF_6) cm^{-1}. NMR ^{1}H: δ 1.90−2.10, 2.30−2.50, 2.80−3.45 (m × 3, 12 H, CH_2), 6.88 (s br, 1 H, C=CH), 7.10−7.65 (m, 25 H, $PC_6H_5 + CC_6H_5$) ppm. ^{13}C{^{1}H}: δ 297.2 (d, CS, $^2J_{CP}$ = 19.7 Hz), 145.7 (s, RuC), 139.6 (s, CPh), 133.9 [d, $C^{2,6}(PC_6H_5)$, $^2J_{CP}$ = 8.9 Hz], 131.0 [$C^4(PC_6H_5)$], 130.9 [d, $C^1(PC_6H_5)$, $^1J_{CP}$ = 45.3 Hz], 130.9 (s, CPh), 128.6 [d, $C^{3,5}(PC_6H_5)$ J_{CP} obscured], 128.4, 127.8, 127.5 [s × 3, $C^{2,3,5,6}(CC_6H_5)$], 127.7 (s, CHPh), 126.3 [$C^1(CHC_6H_5)$], 124.4 [s, $C^4(C_6H_5)$], 101.5, 98.6 (C≡C), 37.2, 35.2, 34.1, 30.4 (s × 4, SCH_2), 34.3 (s br, SCH_2, S *trans* to P), 33.8 (d, SCH_2, S *trans* to P, $^3J_{CP}$ = 5.3 Hz) ppm. ^{31}P{^{1}H}: δ 37.0 ppm. FAB-MS *m*/*z* (% abundance): 791 (100) $[M]^+$, 763 (14) $[M - C_2H_4]^+$, 587 (5) $[M - vinyl]^+$, 560 (12) $[M - C_2H_4 - vinyl]^+$, 501 (6) $[M - C_2H_4 - PPh_3]^+$. Anal. Found: C, 49.8; H, 3.9. Calcd for $C_{41}H_{38}F_6P_2RuS_4 \cdot CH_2Cl_2$: C, 49.4; H, 4.0 (dichloromethane of solvation confirmed by ^{1}H NMR integration).

Preparation of [Ru(η^2-SCCH=CHPh)(PPh$_3$)([9]aneS$_3$)]ClO$_4$ (3·ClO$_4$). $[Ru(CH{=}CHPh)Cl(CS)(PPh_3)_2]$ (200 mg, 0.247 mmol) and [9]aneS_3 (50 mg, 0.277 mmol) were dissolved in dichloromethane (15 mL), and a solution of $LiClO_4$ (200 mg, 1.880 mmol) in water (1 mL) and ethanol (15 mL) was then added. The solution was stirred for 1 h, after which a purple precipitate that had formed was filtered off and washed with ethanol (10 mL) and petroleum ether (10 mL) and dried. Yield: 150 mg (77%). IR (Nujol): 1585, 1565, 1330, 1310, 1279, 1241, 1196, 1089 (ClO_4), 969, 929, 918, 905, 823, 816, 803 cm^{-1}. NMR ^{1}H: δ 1.01, 1.43, 2.21, 2.57, 2.84, 3.10 (m × 6, 12 H, SCH_2), 7.27−7.55 (m, 22 H, PC_6H_5 + CH=CH + C_6H_5) ppm. ^{31}P{^{1}H}: δ 37.3 ppm. FAB-MS *m*/*z* (% abundance): 691 (86) $[M]^+$, 663 (60) $[M - C_2H_4]^+$, 516 (8) $[M - C_2H_4 - SCCH{=}CHPh]^+$, 428 (6) $[M - PPh_3]^+$, 401 (23) $[M - C_2H_4 - PPh_3]^+$. Anal. Found: C, 48.5; H, 4.1. Calcd for $C_{33}H_{34}ClO_4PRuS_4 \cdot 0.5CH_2Cl_2$: C, 48.3; H, 4.2.

(44) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129.
(45) Stille, J. K.; Regan, M. T. *J. Am. Chem. Soc.* **1974**, *96*, 1508.
(46) (a) Clark, G. R.; Roper, W. R.; Wright, L. J.; Yap, V. P. D. *Organometallics* **1997**, *16*, 5135. (b) Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1977**, *142*, C1. (c) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1979**, *182*, C46.
(47) (a) Maitlis, P. M.; Long, H. C.; Quyoum, R.; Turner, M. L.; Wang, Z.-Q. *Chem. Commun.* **1996**, 1. (b) Martinez, J. M.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *Chem. Commun.* **1989**, 286.
(48) Hill, A. F.; Ho, C. T.; Wilton-Ely, J. D. E. T. *Chem. Commun.* **1997**, 2207.
(49) (a) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Shepard, W. E. B.; Wright, L. J. *Chem. Commun.* **1987**, 563. (b) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1989**, *358*, 411.

Preparation of [Ru(η^2-SCCPh=CHPh)(PPh$_3$)([9]aneS$_3$)]ClO$_4$ (4·ClO$_4$). [Ru(CPh=CHPh)Cl(CS)(PPh$_3$)$_2$] (200 mg, 0.226 mmol) and 1,4,7-trithiacyclononane (100 mg, 0.554 mmol) were dissolved in dichloromethane (40 mL) and stirred until all solid had dissolved (ca. 30 min). NaClO$_4$ (60 mg, 0.490 mmol) dissolved in a mixture of water (20 mL) and ethanol (40 mL) was added and the solution stirred for a further 60 min, during which time a purple coloration appeared. After addition of petroleum ether (30 mL) and subsequent partial reduction in solvent volume, purple crystals were obtained and washed with petroleum ether (20 mL) and dried. Yield: 160 mg (82%). IR Nujol: 1581, 1557, 1313, 1258, 1203, 1203, 1143, 1090 (ClO_4−), 998, 934, 905, 845 cm^{-1}. NMR ($CDCl_3$) ^{1}H: δ 0.87, 1.44, 1.83, 2.21, 2.29, 2.51, 2.77, 3.08 (m × 8, 12 H, CH_2), 5.32 (s, 1 H, C=CH), 6.67 [d, C^{2,6}(C_6H_5)], 7.10−7.45 (m, 15 H + 8 H, PC_6H_5 + CC_6H_5) ppm. ^{13}C{^{1}H}: δ 312.8 (d, $^2J_{PC}$ = 9.7 Hz), 149.8, 146.5, 139.1, 135.0, 131.5, 130.8, 129.0, 128.7, 128.6, 128.0 (CPh=CHPh), 134.0 [d, $^1J_{PC}$ = 9.7 Hz, C^{2,6}(PC_6H_5)] 130.6 [d, $^1J_{PC}$ = 42.1 Hz, C^1(PC_6H_5)], 130.3 [C^4(PC_6H_5)], 128.4 [d, $^1J_{PC}$ = 9.7, C^{3,5}(PC_6H_5)], 38.23 (d, $^3J_{PC}$ = 5.4 Hz, SCH_2 *trans* to P), 36.69 (SCH_2), 36.21 (d, $^3J_{PC}$ = 7.5 Hz), 34.12, 32.36, 28.85 (SCH_2) ppm. ^{31}P{^{1}H}: δ 37.2 ppm. FAB-MS *m*/*z* (% abundance): 767 (100) [M]$^+$, 739 (85) [M − C_2H_4]$^+$, 587 (3) [M − CPh=CHPh]$^+$, 516 (13) [M − C_2H_4 − SCCPh=CHPh]$^+$, 477 (30) [M − C_2H_4 − PPh_3]$^+$, 324 (12) [M − [9]aneS$_3$ − PPh_3]$^+$. Satisfactory microanalytical data were not obtained for the perchlorate salt; however metathesis of the counteranion with $NaBPh_4$ provided the tetraphenylborate salt, which analyzed adequately. Anal. Found: C, 64.5; H, 5.0. Calcd for $C_{63}H_{58}BPRuS_4 \cdot 1.25CH_2Cl_2$: C, 64.7; H, 5.1. Dichloromethane solvate confirmed by ^{1}H NMR integration. The corresponding salt [Ru(η^2-SCCR=CHR)(PPh$_3$)([9]aneS$_3$)]Cl (R = C_6H_4Me-4) was similarly prepared from [Ru(CR=CHR)Cl(CS)(PPh$_3$)$_2$] by omitting the halide exchange step. Yield: 86%. IR (Nujol): 1602, 1573, 1503, 1317, 12611180, 1090, 1026. 938, 908, 838, 814 cm^{-1}. NMR ^{1}H: δ 0.88, 1.44, 2.24, 2.73, 3.02, 3.26, 3.47 (m × 7, 12 H, CH_2), 2.27, 2.31 (s × 2, 3 H × 2, CH_3), 6.51, 7.04 (d × 2, 8 H, C_6H_4, $^3J_{HH}$ = 8.2 Hz), 7.31, 7.53 (m × 2, 15 H, C_6H_5), 7.71 (s, 1 H, =CHR) ppm. ^{31}P{^{1}H}: δ 38.0 ppm. Anal. Found: C, 52.4; H, 4.7. Calcd for $C_{41}H_{41}F_6P_2RuS_4$: C, 52.4; H, 4.4.

Preparation of [Os(CH=CHC$_6$H$_4$Me-4)(CS)(PPh$_3$)([9]aneS$_3$)]PF$_6$ (5·PF$_6$). [Os(CH=CHC$_6$H$_4$Me-4)Cl(CS)(BTD)(PPh$_3$)$_2$] (130 mg, 0.124 mmol) and 1,4,7-trithiacyclononane (30 mg, 0.166 mmol) were dissolved in dichloromethane (10 mL), and an ethanolic solution (5 mL) of NH_4PF_6 (40 mg, 0.245 mmol) was added. The reaction was stirred at reflux for 1 h and all solvent evaporated. Diethyl ether (15 mL) was added and a cream solid obtained by ultrasonic trituration. This was filtered, washed with diethyl ether (20 mL) and hexane (20 mL), and dried. Yield: 80 mg (69%). IR (Nujol): 2135, 1977, 1622, 1588, 1298 ν_{CS}, 974, 937, 836 ν_{PF} cm^{-1}. NMR ^{1}H: δ 1.26, 2.10, 2.38, 2.79, 2.87, 3.19 (m × 6, 12 H, SCH_2), 2.28 (s, 3 H, CH_3), 6.59 (d, 1 H, =CH, J_{HH} = 16.8 Hz), 6.84, 7.00 (d × 2, 4 H, C_6H_4, $^3J_{AB}$ = 7.92 Hz), 7.16−7.66 (m, 15 H, PC_6H_5), 7.98 (dd, 1 H, OsCH, J_{HH} = 16.95 Hz, J_{HP} = 4.83 Hz) ppm. ^{31}P{^{1}H}: δ 7.4 ppm. FAB-MS *m*/*z* (% abundance): 795 (32) [M]$^+$, 767 (4) [M − C_2H_4]$^+$, 579 (2) [M − CS − vinyl − 2C_2H_4]$^+$, 503 (2) [M − C_2H_4 − PPh_3]$^+$. Anal. Found: C, 43.7; H, 4.0. Calcd for $C_{34}H_{36}F_6OsP_2S_4$: C, 43.5; H, 3.9.

Preparation of [Ru(C$_6$H$_5$)(CS)(PPh$_3$)([9]aneS$_3$)]PF$_6$ (6·PF$_6$). [Ru(C_6H_5)(CS)Cl(PPh$_3$)$_2$] (200 mg, 0.256 mmol) and 1,4,7-trithiacyclononane (50 mg, 0.277 mmol) were dissolved in a mixture of dichloromethane (25 mL) and ethanol (10 mL). KPF_6 (100 mg, 0.543 mmol) was added as an ethanolic solution (1 mL). The reaction mixture was stirred for 15 h at room temperature, after which all solvent was removed from the red solution. The crude product was dissolved in dichloromethane (10 mL) and filtered through diatomaceous earth to remove precipitated KCl. Ethanol (10 mL) was then added and the solvent volume reduced (rotary evaporator) until precipitation of the red product was complete. The red crystals were washed with ethanol (1 mL) and hexane (10 mL) and dried. Yield: 150 mg (72%). IR (Nujol): 1709, 1567 (C_6H_5), 1293 ν_{CS}, 1015, 1000, 936, 904, 840 (PF_6) cm^{-1}. NMR (CD_2Cl_2) ^{1}H: δ 1.49, 2.03, 2.19, 2.36, 2.48, 2.67, 2.92, 3.13, 3.27, 3.38 (m × 10, 12 H, SCH_2), 6.82 [s br, H^{2,6}(RuC_6H_5)], 7.20−7.50 [m, 18 H, PC_6H_5 and H3−5(RuC_6H_5)] ppm. ^{31}P{^{1}H} (CH_2Cl_2/$CDCl_3$, 3:1): δ 39.4 ppm. FAB-MS *m*/*z* (% abundance): 665 (100) [M]$^+$, 637 (50) [M − C_2H_4]$^+$, 516 (6) [M − C_2H_4 − C_6H_5 − CS]$^+$, 484 (2) [M − [9]aneS$_3$]$^+$, 375 (43) [M − C_2H_4 − PPh_3]$^+$, 347 (10) [M − 2C_2H_4 − PPh_3]$^+$, 319 (14) [M − 3C_2H_4 − PPh_3]$^+$, 279 (34) [Ru[9]aneS$_3$]$^+$. Anal. Found: C, 45.7; H, 3.7. Calcd for $C_{31}H_{32}F_6P_2RuS_4$: C, 46.0; H, 4.0.

Preparation of [Ru(SiMe$_2$OEt)(CS)(PPh$_3$)([9]aneS$_3$)]PF$_6$ (7·PF$_6$). [Ru($SiMe_2OEt$)(CS)Cl(PPh$_3$)$_2$] (200 mg, 0.247 mmol) and [9]aneS$_3$ (50 mg, 0.277 mmol) were dissolved in a mixture of dichloromethane (25 mL) and ethanol (10 mL). KPF_6 (100 mg, 0.543 mmol) was added as an ethanolic solution (1 mL). The red reaction mixture was stirred for 20 h and all solvent removed from the colorless solution. The crude product was dissolved in dichloromethane (10 mL) and filtered through diatomaceous earth. All solvent was again removed and the product precipitated by ultrasonic trituration in diethyl ether (10 mL). The colorless powder was washed with diethyl ether (10 mL) and hexane (10 mL) and dried. Yield: 171 mg (83%). IR (Nujol): 1709, 1408, 1275 ν_{CS} (1269 for 7·BPh$_4$) 1243, 1064, 930, 840 (PF_6) cm^{-1}. NMR ^{1}H: δ 0.02, 0.40 (s × 2, 2 × 3 H, C(CH_3)$_2$), 1.11 (t, 3 H, $CH_2C\underline{H}_3$, J_{HH} = 6.93 Hz), 2.11, 2.32, 2.54, 2.63, 2.78, 3.01, 3.19−3.43 (m × 7, 12 H, SCH_2), 3.48 (q, 2 H, OCH_2, J_{HH} = 7.04 Hz), 7.4−7.6 (m, 15 H, PC_6H_5) ppm. ^{31}P{^{1}H}: δ 36.2 ppm. FAB-MS *m*/*z* (% abundance): 691 (100) [M]$^+$, 663 (8) [M − C_2H_4]$^+$, 588 (3) [M − $SiMe_2OEt$]$^+$, 560 (5) [M − C_2H_4 − $SiMe_2OEt$]$^+$, 428 (3) [M − PPh_3]$^+$, 401 (7) [M − C_2H_4 − PPh_3]$^+$. Anal. Found: C, 41.7; H, 4.7. Calcd for $C_{29}H_{38}F_6OP_2RuS_4Si$: C, 41.7; H, 4.6.

Preparation of [Ru(η^2-SCC$_6$H$_5$)(PPh$_3$)([9]aneS$_3$)]PF$_6$ (8·PF$_6$). [Ru(C_6H_5)(CS)(PPh$_3$)([9]aneS$_3$)]PF_6 (60 mg, 0.074 mmol) was dissolved in tetrahydrofuran (10 mL) and stirred at reflux for 4 h. All solvent was evaporated and the crude product triturated ultrasonically in hexane (20 mL). The dark red-brown product was filtered, washed with hexane (20 mL), and dried. Yield: 52 mg (87%). IR (Nujol): 1585, 1301, 1170, 977, 934, 905, 838 ν_{PF} cm^{-1}. NMR ^{1}H: δ 1.10, 1.33, 1.62, 2.03, 2.26, 2.45, 2.63, 2.92, 3.18 (m × 9, 12 H, SCH_2), 6.81, 6.97 (m × 2, 2 H, CC_6H_5), 7.20−7.70 (m, 18 H, C_6H_5) ppm. ^{31}P{^{1}H}: δ 35.9 ppm. FAB-MS *m*/*z* (% abundance): 665 (29) [M]$^+$, 637 (24) [M − C_2H_4]$^+$, 375 (13) [M − C_2H_4 − PPh_3]$^+$, 263 (10) [PPh_3]$^+$. Anal. Found: C, 45.9; H, 3.9. Calcd for $C_{31}H_{32}F_6P_2RuS_4$: C, 46.0; H, 4.0.

Preparation of [Ru(CH=CHPh)(κ^2-S$_2$CNMe$_2$)(CS)(PPh$_3$)$_2$] (9). A solution of [Ru(CH=CHPh)Cl(CS)(PPh$_3$)$_2$] (160 mg, 0.198 mmol) in dichloromethane (20 mL) was treated with a solution of sodium dimethyldithiocarbamate (500 mg, 3.491 mmol) in water (2 mL) and ethanol (10 mL), prompting an immediate color change (red solution to a yellow one). The solution was stirred for 2 min, after which ethanol (40 mL) was added to precipitate yellow crystals from the green solution. These were filtered and washed with ethanol (10 mL) and petroleum ether (10 mL). Yield: 139 mg (79%). Stability: Good as solid but less than 1 h in solution. IR (Nujol): 1914, 1597, 1585, 1575, 1545, 1512, 1504, 1480, 1432, 1384, 1281, 1251 ν_{CS}, 1141, 1053, 966, 798 cm^{-1}. NMR ^{1}H: δ 2.36, 2.73 (s × 2, 6 H, CH_3), 5.51 (d, 1 H, C$\underline{H}$Ph, J_{HH} = 16.7 Hz), 6.61 [d, 2 H, H^{2,6}(C_6H_5), J_{HH} = 7.6 Hz], 6.89 [t, 1 H, H^4(C_6H_5), J_{HH} = 7.3 Hz], 7.04 [t, 2 H, H^{3,5}(C_6H_5), J_{HH} = 7.3 Hz], 7.29−7.67 (m, 30 H, PC_6H_5), 8.00 (dt, 1 H, RuCH, J_{HH} = 17.2, J_{HP} = 2.3 Hz) ppm. ^{31}P{^{1}H}: δ 36.5 ppm. FAB-MS *m*/*z* (% abundance): 894 (13) [M]$^+$, 789 (22) [M − vinyl]$^+$, 773 (26) [M − S_2CNMe_2]$^+$. Anal. Found: C, 61.2; H, 5.0; N, 1.5. Calcd for $C_{48}H_{43}NP_2RuS_3 \cdot 0.75CH_2Cl_2$: C, 61.2; H, 4.7; N, 1.5.

Preparation of [Ru(CH═CH$_2$)(κ^2-S$_2$CPCy$_3$)(CS)(PPh$_3$)$_2$]PF$_6$ (10·PF$_6$). [Ru(CH═CH$_2$)Cl(CS)(PPh$_3$)$_2$] (200 mg, 0.273 mmol) was dissolved in dichloromethane (10 mL), and S$_2$CPCy$_3$ (107 mg, 0.300 mmol) was added, resulting in an immediate deep red color. Ethanol (5 mL) was added along with NH_4PF_6 (90 mg, 0.552 mmol) in water (1 mL) and ethanol (5 mL). The solution was stirred for 2 h and the solvent volume then reduced (rotary evaporator) until precipitation of a purple solid was observed. This was filtered off and washed with ethanol (10 mL) and petroleum ether (20 mL) and dried. Yield: 242 mg (74%). IR (Nujol): 1716, 1586, 1551, 1267 ν_{CS}, 1237, 967, 919, 840 (PF_6) cm^{-1}. NMR ^{1}H: δ 0.09−2.15 (m, 33 H, Cy), 4.36 (dt, 1 H, H$_\beta$, $J_{H\alpha H\beta}$ = 17.8, $J_{H\beta' H\beta}$ = 2.1 Hz), 5.39 (dt, 1 H, H$_{\beta'}$, $J_{H\alpha H\beta'}$ = 10.4, $J_{H\beta H\beta'}$ = 2.5 Hz), 7.32−7.55 (m, 30 H, PC$_6$H$_5$), 7.65 (ddd, 1 H, H$_\alpha$, $J_{H\alpha H\beta}$ = 11.8, $J_{H\alpha P}$ = 6.7, $J_{H\alpha H\beta'}$ = 1.5 Hz) ppm. ^{31}P{^{1}H}: δ 36.7, 31.8 ppm. FAB-MS *m*/*z* (% abundance): 1053 (21) [M]$^+$, 791 (72) [M − PPh$_3$]$^+$, 763 (4) [M − vinyl − PPh$_3$]$^+$, 697 (3) [M − S$_2$CPCy$_3$]$^+$, 433 (5) [M − S$_2$CPCy$_3$ − PPh$_3$]$^+$. Anal. Found: C, 55.5; H, 5.9. Calcd for C$_{58}$H$_{66}$F$_6$P$_4$RuS$_3$·CH$_2$Cl$_2$: C, 55.2; H, 5.3.

Computational Details. Models used PH_3 in place of PPh_3. Because ligands must rotate 90° from **1** to **1TS** so that the π-system is aligned toward the CS, full phosphines would incur higher reaction barriers, particularly for **1TSb**,**d**, which bear ═CHPh moieties *syn* to the phosphine. In this respect, we have previously identified C−H···π interactions between arylphosphine and vinyl ligands.[50] Calculations were performed using density functional methods of the Amsterdam Density Functional (ADF v2006.01)[51−54] with the generalized gradient approximation and the local density approximation of Vosko, Wilk, and Nusair,[55] with Becke88[56] and Perdew86[57] electron exchange and correlation corrections. The basis sets used were uncontracted triple-ζ Slater-type orbitals (STOs) with polarization functions, labeled TZP in ADF. Scalar relativistic effects were included with the ZORA formalism. The cores of atoms were frozen: C, N, O, and F up to the 1s level, P and S up to the 2p level, and Ru up to the 3d level. Minima **1a**−**f** and **3a**−**f** have been verified by full frequency calculations. Although some possessed an imaginary eigenvector in the Hessian, these were visually confirmed to correspond with very flat motions on the potential energy surface; reoptimization at higher convergence criteria could resolve these, but would not significantly lower any energies. **1g**−**m** and **3g**−**m** were derived from **1c** and **3c** and underwent full geometry optimization. Guess structures for **1TSa**−**e** were found by reoptimizing **1** while fixing the R−CS distance at decreasing intervals; the maxima along these linear transits were used in transition-state searches. Guess structures for **1TSg**−**m** were derived from **1TSc**, and the substituents were optimized prior to initiating transition-state searches. All transition states possessed an imaginary frequency vibration corresponding with formation of the R−CS bond. Some also possessed a second, lower-energy imaginary frequency. Intermediates **2a**−**e** were determined by geometry optimization of the extremes of the corresponding imaginary frequency vibrations of **1TSa**−**e**, but all possessed their own imaginary frequency vibration, suggesting a nearly barrierless isomerization to **3**. As such, transition states from **2** to **3** were not found, and **1TS** is assumed to determine the overall reaction barrier.

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Supporting Information Available: Full symmetry-adapted fragment orbital gross populations and all Cartesian coordinate files (.xyz) for the structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(50) Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, *17*, 4249.
(51) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84.
(52) Fonseca Guerra, C.; Snijders, J. G.; Velde, G. T.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391.
(53) (a) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; Van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.
(54) *SCM, version 2006 01*; Theoretical Chemistry, Vrije Universiteit, Amsterdam, 2000,
(55) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys* **1980**, *58*, 1200.
(56) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(57) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.