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Communications

Organometallic Macrocycle Chemistry. 2. Synthesis of Organometallic (Trithiacyclononane)ruthenium(II) Complexes

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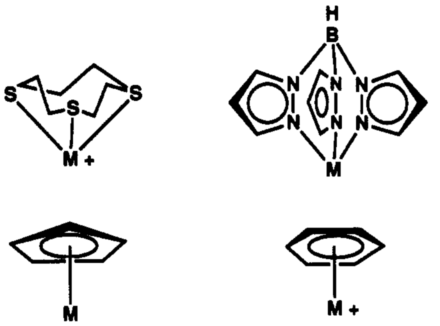
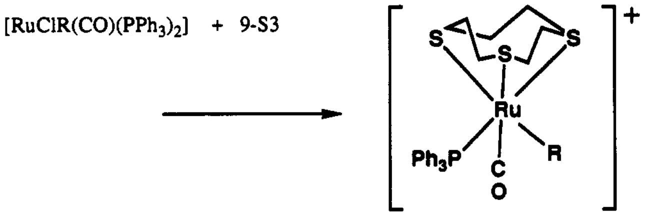
Summary: The reactions of 1,4,7-trithiacyclononane (9-S3) with the coordinatively unsaturated σ-vinyl complexes [Ru(CH=CHR)Cl(CO)(PPh$_3$)$_2$] (R = H, C_4H_9, C_6H_4Me-4) proceed with loss of a chloride and a phosphine ligand from the coordination sphere to provide the salts [Ru(CR=CHR)(CO)(PPh$_3$)(9-S3)]Cl (isolated as AsF_6^- salts) in high yield. Similar treatment of the complex [Ru(C_6H_4Me-4)Cl(CO)(PPh$_3$)$_2$] leads to the related σ-tolyl derivative [Ru(C_6H_4Me-4)(CO)(PPh$_3$)(9-S3)]Cl. The analogous reactions of 9-S3 with the related thiocarbonyl complexes [Ru(CR=CHPh)Cl(CS)(PPh$_3$)$_2$] (R = H, Ph) and [Ru{C(CO$_2$Me)=CHCO$_2$Me}Cl(CS)(PPh$_3$)$_2$] provide the cationic complexes [Ru(η^2-SCCR=CHR)(PPh$_3$)(9-S3)]$^+$ and [Ru{C(CO$_2$Me)=CHCO$_2$Me}(CS)(PPh$_3$)(9-S3)]$^+$, the former via vinyl–thiocarbonyl ligand coupling.

The chemistry of polythia macrocycles, the sulfur analogues of crown ethers, has been primarily preoccupied with complexes bearing typically "innocent" ligands, e.g., halides, carbonyls, η^n-C_nH_n groups, etc.[1] We are currently attempting to develop the organometallic chemistry of complexes bearing 1,4,7-trithiacyclononane (9-S3) ligands, in part to investigate the analogy between 9-S3, cyclopentadienyl, η^6-arene, and κ^3-HB(pz)$_3$ (pz = pyrazol-1-yl) ligands (Chart I). We report herein the simple synthesis of a class of σ-vinyl and σ-aryl complexes of ruthenium(II), bearing carbonyl or thiocarbonyl ligands.

Chart I. Six-Electron *fac* Ligands



Scheme I. Reactions of Ruthenium Phosphine Complexes with 9-S3 (R = C_6H_4Me, CH=CHPh, CPh=CHPh)



The 16-electron σ-(*E*)-vinyl complexes [Ru(CH=CHR)Cl(CO)(PPh$_3$)$_2$] (R = H, C_4H_9, C_6H_4Me-4)[2] react with 9-S3 in dichloromethane solution with displacement of one phosphine and the chloride ligand. The salts [Ru(CH=CHR)(CO)(PPh$_3$)(9-S3)]Cl (R = H (1), C_4H_9 (2), C_6H_4Me-4 (3)) are formed in essentially quantitative yield and may be metathesized with sodium hexafluoroarsenate to provide the AsF_6 derivatives. The gross formulation follows from the appearance of molecular ions in the FAB mass

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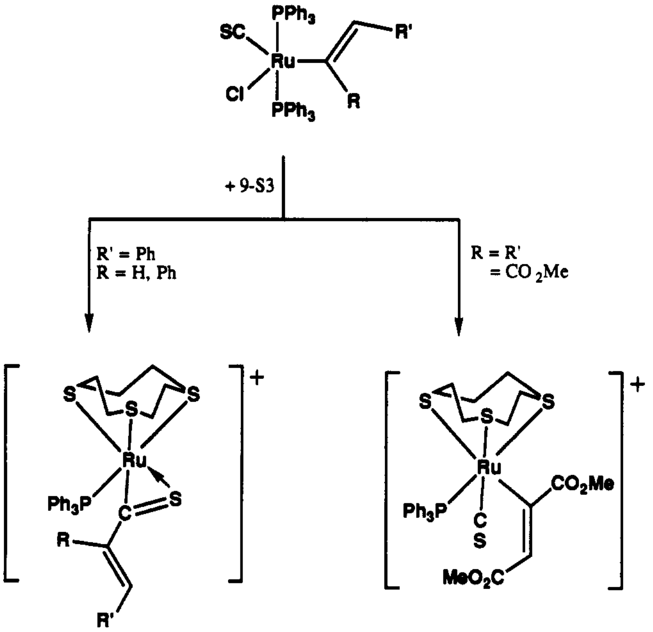
(1) Cooper, S.; Rawle, S. C. *Struct. Bonding* **1990**, *72*, 1.

(2) Torres, M. R.; Vegas, A.; Santos, A. *J. Organomet. Chem.* **1986**, *309*, 169.

0276-7333/92/2311-2323$03.00/0

Scheme II. Reactions of Ruthenium Thiocarbonyl Complexes with 9-S3



spectra of the complexes. The spectroscopic data for the complexes[3] feature single carbonyl-associated infrared absorbances in the region 1960–1980 cm^{-1}, while the trans β-vinyl group is evident from the appearance of AB quartets in the ^1H NMR spectra of the derivatives **2** and **3**. COSY and NOE ^1H NMR experiments on $[Ru(CH{=}CHC_6H_4Me\text{-}4)(CO)(PPh_3)(9\text{-}S3)]Cl$ show that the molecule is static on the ^1H NMR time scale. The σ-aryl derivative $[Ru(C_6H_4Me\text{-}4)(CO)(PPh_3)(9\text{-}S3)]Cl$ (**4**) is readily prepared from the corresponding tolyl complex $[Ru(C_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$,[4] and spectroscopic data[3] indicate that it is isostructural with the vinyl derivatives.

The thiocarbonyl ligand shows an enhanced propensity to enter into migratory insertion reactions, relative to coordinated CO.[5] The reactions of the recently prepared thiocarbonyl complexes $[Ru(CR{=}CHR)Cl(CS)(PPh_3)_2]$ (R = H, Ph) and $[Ru\{C(CO_2Me){=}CHCO_2Me\}Cl(CS)(PPh_3)_2]$[6] were therefore of interest. Treating these complexes with 9-S3 in the presence of $LiClO_4$ leads to formation of the purple thiocinnamoyl complexes $[Ru(\eta^2\text{-}SCCR{=}CHR)(PPh_3)(9\text{-}S3)]^+$ or the yellow σ-vinyl species $[Ru\{C(CO_2Me){=}CHCO_2Me\}(CS)(PPh_3)(9\text{-}S3)]^+$ (Scheme II). The observation of a migratory insertion coupling in the former complexes is unusual in that ancillary π-acid ligands are normally required for such a reaction to occur;[6] e.g., reaction of $[Ru(CH{=}CHPh)Cl(CS)(PPh_3)_2]$ with sodium dimethyldithiocarbamate fails to induce such a reaction, providing rather the octahedral σ-vinyl complex $[Ru(CH{=}CHPh)(S_2CNMe_2)(CS)(PPh_3)_2]$.[6] The failure of $[Ru\{C(CO_2Me){=}CHCO_2Me\}(CS)(PPh_3)(9\text{-}S3)]^+$ to isomerize to the thioacyl tautomer presumably reflects enhanced Ru–C bond strength for the vinyl ligand.

We are currently investigating the reactivity of these complexes in parallel studies of the related neutral hydrotris(pyrazolyl)borato derivatives $[RuR(CO)(PPh_3)\{HB(pz)_3\}]$ (pz = pyrazol-1-yl).[7] Consistent with the cationic nature of the 9-S3 derivatives, the carbonyl stretching frequencies for the compounds appear ca. 30 cm^{-1} to higher energy and the ^1H chemical shifts of the vinylic protons ($RuCR{=}CHR$) are moved ca. 1 ppm to lower field of those observed for the hydrotris(pyrazolyl)borato analogues.

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[3] Data for $[Ru(CH{=}CHC_6H_4Me\text{-}4)(CO)(PPh_3)(9\text{-}S3)]AsF_6$: IR (Nujol) 1970 cm^{-1} (ν_{CO}); ^1H NMR ($CDCl_3$, 25 °C) 1.70, 2.10, 1.59, 2.82, 2.92, 2.96, 3.13 [m × 7, 12 H, 9-S3], 2.27 [s, 3 H, $C_6H_4CH_3$], 6.96, 6.78 [$(AB)_2$, 4 H, $C_6H_4CH_3$, $J(AB)$ = 8.0 Hz], 6.54, 7.29 [AB, 1 H, $P_2RuCH_A{=}CH_BC_6H_4Me$, $J(AB) = 16.0$, $J = (PH_A) = 16.8$ Hz], 7.40–7.51 ppm [m, 15 H, PC_6H_5]; ^{31}P NMR ($CDCl_3$, 25 °C) 40.6 ppm; FAB-MS (nba) *m/e* 689 (M^+), 515 ($[M - (9\text{-}S3)]^+$). Anal. Calcd for $C_{31}H_{36}AsF_6S_3OPRu$: C, 49.8; H, 4.1. Found: C, 49.9; H. 4.1. Data for $[Ru(\eta^2\text{-}SCCH{=}CHC_6H_5)(PPh_3)(9\text{-}S3)]ClO_4$: IR (Nujol) 1585 s, 1566 s cm^{-1} (vinyl); ^1H NMR ($CDCl_3$, 25 °C) 1.03, 1.44, 2.15, 2.26, 2.51, 2.59 [m × 6, 1 H × 6, 9-S3], 2.84, 3.09 [m × 2, 6 H, 9-S3], 7.19–7.54 ppm [m, 15 H, PC_6H_5 and CC_6H_5]; FAB-MS *m/e* 691 (M^+) (no significant fragmentation). Anal. Calcd for $C_{33}H_{34}ClO_4PRuS_4\cdot0.5CH_2Cl_2$: C, 48.3; H, 4.2. Found: C, 47.9; H, 4.1. Data for $[Ru\{C(CO_2Me){=}CHCO_2Me\}(CS)(PPh_3)(9\text{-}S3)]ClO_4$: IR (Nujol) 1724 s, 1714 sh (CO_2Me), 1570 (vinyl), 1290 vs (CS); ^1H NMR ($CDCl_3$, 25 °C) 2.09, 2.27 [m × 2, 1 H × 2, 9-S3], 2.82, 3.19, 3.35 [m × 3, 10 H, 9-S3], 3.51, 3.75 [s × 2, 6 H, CO_2CH_3], 5.38 [s (br), 1 H, $=CHCO_2Me$], 7.37–7.53 ppm [m, 15 H, PC_6H_5]; FAB-MS (nba) *m/e* 731 (M^+) (no significant fragmentation). Anal. Calcd for $C_{28}H_{34}ClO_8PRuS\cdot2CH_2Cl_2$: C, 43.3; H, 4.0. Found: C, 43.6; H, 3.9.

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[5] Clark, G. R.; Collins, T. J.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1978**, *157*, C23. Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1977**, *139*, C56. Elliott, G. P.; Roper, W. R. *J. Organomet. Chem.* **1985**, *250*, C5. For a recent review of metal thiocarbonyl chemistry, see: Broadhurst, P. V. *Polyhedron* **1985**, *4*, 1801.

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