bleaching of the starting dimer due to formation of $Mn(CO)_5$ radicals is not a factor.

Examination of similar samples in the IR revealed the presence of substantial solvento form at the shorter time and its complete absence at the longer time. Most strikingly, the spectra in Figure 3 demonstrate that there is little difference in the absorption spectra of the solvento and semibridged forms. In particular, there is very little absorbance difference in the vicinity of 480 nm and virtually no absorbance due to either species at 580 nm or longer wavelength. Thus, the UV–visible absorbances at these wavelengths do not afford an effective means of determining whether the solvento or semibridged form is present.

The transient IR spectrum of $Mn_2(CO)_9$ following laser flash photolysis at room temperature has been reported by Church and co-workers.[8b] Bands due to $Mn_2(CO)_8(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CO)$ are observed at short times, on the order of 10 μs. Assuming from this result that the rate constant for semibridge formation from the solvento species is 1×10^6 s^{-1} or faster at room temperature, the enthalpy of activation for semibridge formation is on the order of 5 kcal mol^{-1} or larger. The estimated barrier to semibridge formation is similar to the rough estimate of 8 kcal mol^{-1} for the free energy barrier to formation of the semibridge in the phosphine-substituted CO-loss species $Mn_2(CO)_7[P(n\text{-}Bu)_3]_2$, on the basis of room-temperature kinetics behavior.[13] While these estimates are crude, they are reasonably consistent and suggest that formation of $Mn_2(CO)_8(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CO)$ following photodissociation of CO at room temperature could be fairly slow, in the time range of 0.01–1 μs. The most promising approach to determination of the time scale for semibridge formation at room temperature would seem to be time-resolved IR detection.

Acknowledgment. This research was supported by Grant No. NSFCHE89-12773 from the National Science Foundation.

OM9204853

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Migratory Insertion of Silyl and Thiocarbonyl Ligands on Ruthenium and Osmium To Give the η^2-Silathioacyl Complexes $M(\eta^2\text{-}C[S]SiMe_2X)Cl(CO)(PPh_3)_2$ (M = Ru, Os; X = Cl, OEt)

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Summary: The yellow, coordinatively unsaturated silyl thiocarbonyl complexes of ruthenium and osmium $M(SiMe_2Cl)Cl(CS)(PPh_3)_2$ (M = Ru (**1a**), Os (**2a**)) can be prepared by reaction of $HSiMe_2Cl$ with $MHCl(CS)(PPh_3)_3$ or $MPhCl(CS)(PPh_3)_2$. The Si–Cl bond in **1a** and **2a** is readily cleaved by ethanol, and the corresponding ethoxysilyl complexes **1b** and **2b** are formed. Addition of CO to **1a**, **1b**, and **2b** induces an immediate migratory insertion reaction involving the silyl and thiocarbonyl ligands, and the novel η^2-silathioacyl complexes $M(\eta^2\text{-}C[S]SiMe_2X)Cl(CO)(PPh_3)_2$ (M = Ru, X = OEt (**1c**), Cl (**1d**); M = Os, X = OEt (**2c**)) are formed. The single-crystal X-ray structure determination of **1c** is described.

Migratory insertion reactions involving coordinated alkyl and carbonyl ligands are well-known and have been studied extensively.[1] In contrast, the first examples of the analogous reaction involving silyl and carbonyl ligands have been reported only recently.[2] To date, all examples of this latter reaction have involved early transition metals of d^0 electron configuration with the resulting silaacyl ligands coordinating in a η^2 fashion through oxygen as well as carbon.[3] Although the known carbonyl silyl derivatives of the later transition metals are reluctant to undergo migratory insertion,[4] it appeared to us that the related thiocarbonyl derivatives would be much more likely to react in this way. The thiocarbonyl ligand generally undergoes migratory insertion reactions more readily than carbonyl (even hydride migration is easily induced), and for the later, thiophilic transition metals, coordination of the thioacyl ligand in a η^2 fashion might provide additional stability to the rearranged products.[5a,b] We therefore synthesized mixed silyl thiocarbonyl complexes of ruthenium and osmium (**1a**,**b** and **2a**,**b**) and now report the first examples of migratory insertion involving these ligands to give the corresonding η^2-silathioacyl derivatives.

We have previously reported that reaction of the silanes $HSiR_3$ (R = Cl, Me, Et) with the coordinatively unsaturated σ-aryl complexes $MPhCl(CO)(PPh_3)_2$ (M = Ru, Os) provides a simple and efficient route to the corresponding silyl derivatives $M(SiR_3)Cl(CO)(PPh_3)_2$.[6] In an extension

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(2) Woo, H.-G.; Freeman, W. P.; Tilley, T. D. *Organometallics* **1992**, *11*, 2198 and references therein.

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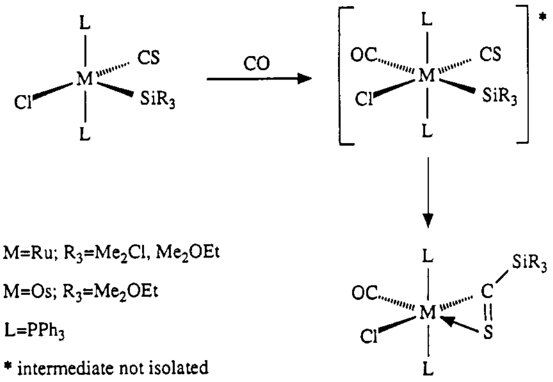
Table I. Selected Spectral Data for Compounds 1a–d and 2a–c

	IR[b]				NMR[c]	
compd[a]	CS	CO	$SiMe_2X$	$C[S]SiMe_2X$	^{31}P[d]	^1H
$Ru(SiMe_2Cl)Cl(CS)(PPh_3)_2$ (**1a**)	1271		883, 801		31.07	0.64 (s, 6 H, $Si(CH_3)_2$)
$Ru(SiMe_2OEt)Cl(CS)(PPh_3)_2$ (**1b**)	1276		1063, 926, 831, 803		32.38	3.35 (q, 2 H, CH_2, $^3J(HH)$ 6.98); 0.74 (t, 3 H, CH_3, $^3J(HH)$ 6.98); 0.36 (s, 6 H, $Si(CH_3)_2$)
$Ru(\eta^2\text{-}C[S]SiMe_2OEt)Cl(CO)(PPh_3)_2$ (**1c**)		1912		1250, 1073, 952, 840, 816 781	34.66	3.70 (q, 2 H, CH_2, $^3J(HH)$ 6.97); 1.29 (t, 3 H, CH_3, $^3J(HH)$ 6.97); −0.35 (s, 6 H, $Si(CH_3)_2$)
$Ru(\eta^2\text{-}C[S]SiMe_2Cl)Cl(CO)(PPh_3)_2$ (**1d**)		1921		1254, 839, 812, 789	33.19	−0.19 (s, 6 H, $Si(CH_3)_2$)
$Os(SiMe_2Cl)Cl(CS)(PPh_3)_2$ (**2a**)	1287		833, 801		21.58	0.58 (s, 6 H, $Si(CH_3)_2$)
$Os(SiMe_2OEt)Cl(CS)(PPh_3)_2$ (**2b**)	1283		1071, 935, 825, 802		23.10	3.31 (q, 2 H, CH_2, $^3J(HH)$ 7.00); 0.70 (t, 3 H, CH_3, $^3J(HH)$ 7.00); 0.26 (s, 6 H, $Si(CH_3)_2$)
$Os(\eta^2\text{-}C[S]SiMe_2OEt)Cl(CO)(PPh_3)_2$ (**2c**)		1908, 1894[e]		1247, 1071, 942, 926, 836, 813, 780	11.47	3.72 (q, 2 H, CH_2, $^3J(HH)$ 6.97); 1.30 (t, 3 H, CH_3, $^3J(HH)$ 6.97); −0.36 (s, 6 H, $Si(CH_3)_2$)

[a] Satisfactory elemental analyses were obtained for all new compounds. [b] Nujol mull (cm^{-1}); $\nu(CO)$ and $\nu(CS)$ very strong. [c] $CDCl_3$; $^3J(HH)$ in Hz; δ in ppm; TMS at δ 0 (^1H NMR), H_3PO_4 at δ 0, external standard (^{31}P NMR). [d] All singlets. [e] Single absorbance in CH_2Cl_2 solution at 1900 cm^{-1}.

Scheme I



of this work we have now found that the related yellow thiocarbonyl complexes $M(SiMe_2Cl)Cl(CS)(PPh_3)_2$ (M = Ru (**1a**), Os (**2a**)) can be prepared from reaction of $MPhCl(CS)(PPh_3)_2$ with $HSiMe_2Cl$.[5a,7] Compounds **1a** and **2a** can also be prepared by reaction of the hydrido complexes $MHCl(CS)(PPh_3)_3$ with $HSiMe_2Cl$ directly.[5b,c,7] For compound **1a**, this latter reaction represents a superior synthetic route.

Selected spectral data for compounds **1a** and **2a** (and all other new compounds) are collected in Table I. The structures of these compounds are most likely square pyramidal with the silyl group in the apical position and the two PPh_3 ligands mutually trans. This arrangement was found for the closely related five-coordinate silyl complexes $Ru(SiR_3)Cl(CO)(PPh_3)_2$ (R = Et, OEt) and $Os(SiMe_3)Cl(CO)(PPh_3)_2$.[6] The single resonance observed in the ^{31}P NMR spectrum of each of these compounds is consistent with such an arrangement.

The Si–Cl bond in **1a** is reactive, and the corresponding ethoxysilyl derivative $Ru(SiMe_2OEt)Cl(CS)(PPh_3)_2$ (**1b**) rapidly forms upon addition of ethanol to a dichloromethane solution of **1a**.[8] The ethoxy substituent on silicon is clearly evident in the ^1H NMR and IR spectra of **1b** (Table I). The osmium complex **2a** also reacts with ethanol to form the analogous osmium ethoxysilyl derivative $Os(SiMe_2OEt)Cl(CS)(PPh_3)_2$ (**2b**).

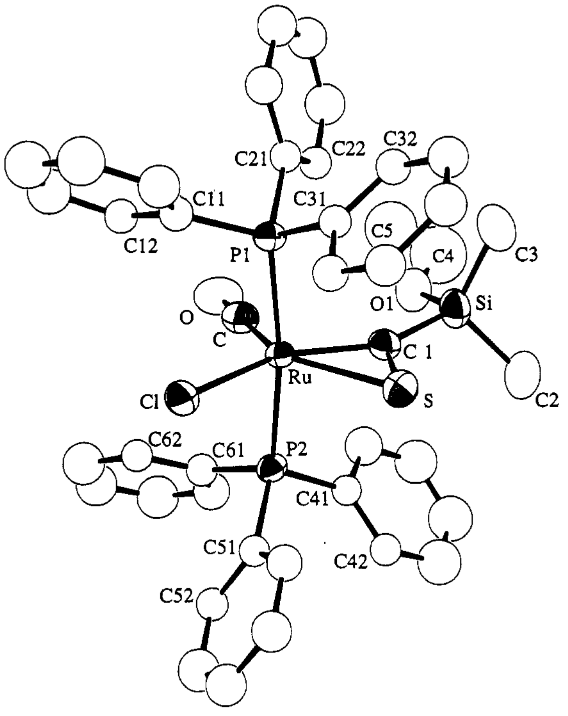


Figure 1. ORTEP view of **1c** with thermal ellipsoids at the 50% probability level. Selected distances (Å) and angles (deg): Ru–C(1), 1.978 (8); Ru–S, 2.545 (2); C(1)–S, 1.637 (8); C(1)–Si, 1.885 (8); Ru–C(1)–S, 89.0 (4); Ru–S–C(1), 51.0 (3); S–Ru–C(1), 40.0 (2); Ru–C(1)–Si, 147.4 (4); C–Ru–C(1), 106.6 (3); C–Ru–Cl, 109.3 (3); Cl–Ru–S, 104.1 (1).

As might be expected, carbon monoxide rapidly adds to the coordinatively unsaturated compound **1b**. However, at room temperature the addition is immediately followed by a migratory insertion reaction involving the mutually cis thiocarbonyl and silyl ligands[9,10] (Scheme I) and the corresponding red η^2-silathioacyl complex $Ru(\eta^2\text{-}C[S]SiMe_2OEt)Cl(CO)(PPh_3)_2$ (**1c**) is formed.[11] Similarly, **1d**

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[7] $HSiMe_2Cl$ (0.200 g, 2.0 mmol) was introduced into a solution of $RuHCl(CS)(PPh_3)_3$ (0.100 g, 0.10 mmol) in dry toluene (10 mL) in a Schlenk tube, which was then sealed. The solution was heated to 80 °C with stirring for 1 h. The resulting yellow solution was evaporated to a small volume under reduced pressure and then dry hexane added to effect crystallization of the pure, yellow-orange $Ru(SiMe_2Cl)Cl(CS)(PPh_3)_2$ (0.076 g, 92%; mp 136–140 °C). Using similar conditions, reaction of $HSiMe_2Cl$ with $OsPhCl(CS)(PPh_3)_2$ or $OsHCl(CS)(PPh_3)_3$ gave $Os(SiMe_2Cl)Cl(CS)(PPh_3)_2$ (ca. 75% yield in both cases, mp 128–130 °C).

[8] $Ru(SiMe_2Cl)Cl(CS)(PPh_3)_2$ (**1a**; 0.160 g) was dissolved in dichloromethane (20 mL), ethanol (10 mL) added, and the resulting solution stirred at room temperature for 1 min. Reduction of the solvent volume under reduced pressure then afforded yellow crystals of $Ru(SiMe_2OEt)Cl(CS)(PPh_3)_2$ (**1b**; 0.130 g, 80%; mp 173–175 °C). Treatment of **2a** in a similar manner yielded **2b**.

[9] Carbonylation of $M(SiR_3)Cl(CO)(PPh_3)_2$ (M = Ru, Os) gives the corresponding dicarbonyl derivatives, which do not rearrange to silaacyl products: Roper, W. R.; Salter, D. M.; Wright, L. J. To be submitted for publication.

[10] In a parallel reaction carbonylation of the *p*-tolyl complex of osmium $Os(p\text{-tolyl})Cl(CS)(PPh_3)_2$ produces $Os(p\text{-tolyl})Cl(CO)(CS)(PPh_3)_2$, which can be isolated as a white, crystalline solid before rearrangement to the red η^2-thioacyl complex $Os(\eta^2\text{-}C[S]\text{-}p\text{-tolyl})Cl(CO)(PPh_3)_2$ occurs.[5a]

and **2c** are formed on carbonylation of **1a** and **2b**, respectively.

The structure of $Ru(\eta^2\text{-}C[S]SiMe_2OEt)Cl(CO)(PPh_3)_2$ (**1c**) has been determined by a single-crystal X-ray diffraction study,[12] and an ORTEP diagram is shown in Figure 1. The coordination geometry about ruthenium can be considered as a distorted octahedron with the two PPh_3 ligands axial and the carbonyl, chloride, and η^2-silathioacyl ligands all equatorial and coplanar with ruthenium. The Ru–C(1) distance of 1.978 (8) Å is slightly shorter than the Ru–C(sp^2) single-bond length of 2.056 (3) Å in $Ru(p\text{-tolyl})Cl(CO)(PPh_3)_2$,[13] and the C(1)–S distance of 1.637 (8) Å is midway between expected values for related carbon–sulfur double (1.55–1.56 Å) and single bonds (1.79–1.86 Å).[5a] The Ru–S distance of 2.545 (2) Å is longer than that typically found for Ru–S bonds.[14] These values can all be compared with those found in the η^1-arylthioacyl complex of osmium $Os(\eta^2\text{-}C[S]\text{-}p\text{-tolyl})(\eta^1\text{-}O_2CCF_3)(CO)(PPh_3)_2$.[5a] Here Os–C (1.91 (2) Å) and Os–S (2.513 (6) Å) are both shorter while C–S is longer (1.72 (2) Å) than the corresponding distances in **1c**.

The results provide a good illustration of the usefulness of the thiocarbonyl ligand in observing otherwise difficult migratory insertion reactions. Further elaboration of these group 8 silathioacyls through electrophilic addition to the S atom is under study.

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Supplementary Material Available: Text giving elemental analysis and melting point data for compounds prepared in this paper and tables of crystal data (containing details of the data collection and structure solution), positional and thermal parameters, and bond distances and angles for **1c** (9 pages). Ordering information is given on any current masthead page.

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(11) $Ru(SiMe_2OEt)Cl(CS)(PPh_3)_2$ (**1b**; 0.100 g) was dissolved in benzene (15 mL) at room temperature and CO gas at atmospheric pressure bubbled through the stirred solution for approximately 20 s. The resulting red solution was evaporated to a low volume under reduced pressure and hexane slowly added to effect crystallization. Recrystallization from benzene/hexane yielded red crystals of $Ru(\eta^2\text{-}C[S]\text{-}SiMe_2OEt)Cl(CO)(PPh_3)_2$ (**1c**; 0.083 g, 81%; mp 171–173 °C). Treatment of **1a** and **2b** in a similar manner yielded **1d** and **2c**, respectively.

(12) Red crystals of **1c** were grown from benzene/ethanol. Crystal data: $a = 35.285$ (7) Å, $b = 10.399$ (5) Å, $c = 24.116$ (4) Å, $\beta = 116.02$ (2)°, $Z = 8$, $D_{calc} = 1.370$ g cm^{-3}, space group $C2/c$. A total of 3495 reflections ($I > 3\sigma(I)$) were collected on a Nonius CAD-4 diffractometer at 293 K using Mo Kα radiation ($\lambda = 0.71069$). Least-squares refinement converged to $R(F) = 0.047$ and $R_w(F) = 0.045$.

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Catalytic Activity of a Well-Defined Binuclear Ruthenium Alkylidene Complex[†]

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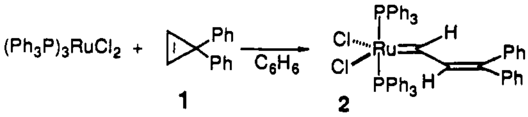
Summary: The reaction of $[Cp^*RuCl]_4$ with 1,1-diphenylcyclopropene (**1**) gives the bridging vinyl carbene complex $[Cp^*RuCl]_2{=}CHCH{=}CPh_2$ (**4**) in moderate yield. This material selectively catalyzes the dimerization of **1** to the triene $Ph_2C{=}CHCH{=}CHCH{=}CPh_2$. Complex **4** polymerizes norbornene by a ring-opening metathesis process despite the bridging nature of the alkylidene.

Recent developments in our laboratories on the synthesis of well-defined, ruthenium-based olefin metathesis catalysts have stemmed from investigations of the reactivity of 1,1-diphenylcyclopropene (1) with ruthenium(II) sources, (e.g. eq 1).[1,2] In an effort to expand upon the base of ruthenium complexes capable of metathesis, the reactivity of $(Cp^*RuCl)_4$[3] ($Cp^* = \eta^5\text{-}C_5Me_5$; **3**) with **1**[4] was investigated.



1 **2** (1)

Preparative-scale reaction of **3** with 8 equiv of **1** (2 equiv per Ru center) leads to clean formation of a crystalline

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[†] Contribution No. 8680 from the California Institute of Technology; Contribution No. 6349 from Du Pont.

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