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Syntheses and reactions of metal carbonyl complexes containing the trimethylsilylmethyl ligand; CO insertion reactions assisted by the trimethylsilylmethyl groups

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Abstract

Trimethylsilylmethyl complexes of ruthenium and tungsten, $Cp(CO)_2RuCH_2SiMe_3$ (**1**) ($Cp = \eta^5$-C_5H_5) and $Cp(CO)_3WCH_2SiMe_3$ (**2**) were prepared by reactions of $ClMgCH_2SiMe_3$ with $Cp(CO)_2RuCl$ and $Cp(CO)_3WCl$ respectively, in ether at low temperature. The complex $(CO)_5ReCH_2SiMe_3$ (**3**) was prepared by reaction of ICH_2SiMe_3 with $NaRe(CO)_5$ in THF. In contrast to the severe conditions required for the CO insertion reactions of $Cp(CO)_2RuCH_3$ and $Cp(CO)_3WCH_3$, carbonylation reactions of **1** and **2** with PPh_3 took place readily under mild conditions and gave two acyl complexes $Cp(CO)(PPh_3)RuC(O)CH_3$ (**4**) and $Cp(CO)_2(PPh_3)WC(O)CH_3$ (**5**) respectively. The reaction of **3** with PPh_3 in CD_3CN retained the trimethylsilyl group and gave both the acyl product $(CO)_4(PPh_3)ReC(O)CH_2SiMe_3$ (**6**) and the substitution product $(CO)_4(PPh_3)ReCH_2SiMe_3$ (**7**). The CO insertion reactions of these three complexes are believed to be assisted by the M–C–Si angles being rather larger. The Ru–C–Si angle of **1** is 119°.

Complexes **1** and $\mathbf{5} \cdot 1.5C_6H_6$ were confirmed by X-ray crystallography: Crystal data for **1**: space group $P\bar{1}$, $a = 6.933(1)$ Å, $b = 8.455(1)$ Å, $c = 12.001(1)$ Å, $\alpha = 105.88(1)°$, $\beta = 98.41(1)°$, $\gamma = 92.55(1)°$, $V = 666.7$ Å^3, $Z = 2$; $R(F) = 0.0296$, $R_w(F) = 0.0254$, based on 4586 reflections with $I > 3\sigma(I)$. Crystal data for **5**: space group $P\bar{1}$, $a = 8.922$ (2) Å, $b = 13.496(2)$ Å, $c = 13.925(2)$ Å, $\alpha = 102.94(1)°$, $\beta = 109.71(2)°$, $\gamma = 87.13(1)°$, $V = 1537.9$ Å^3, $Z = 2$; $R(F) = 0.0253$, $R_w(F) = 0.0190$, based on 4596 reflections with $I > 3\sigma(I)$. The other complexes were characterized by spectroscopic studies.

1. Introduction

CO insertion reaction is a key step in homogeneous catalysis and in the synthesis of organometallic compounds [1]. Factors known to govern the rate of CO insertion reaction include the entering ligand, solvent and alkyl group. Rather limited information is available on how the nature of the alkyl group affects the rate of CO insertion. Metal carbonyl complexes with methyl ligands show reduced rates of insertion as additional electron-withdrawing substituents are added. However, other factors may also make a substantial difference in the reaction rate [1b].

In a dinuclear ruthenium-methylene complex [2], $[Cp(CO)_2Ru]_2(\mu$-$CH_2)$, a facile CO insertion under relatively mild conditions (25°C, 40 psi CO) was observed. In contrast to this complex, ruthenium methyl complex and its analogues [3] *e.g.*, $Cp(CO)_2RuCH_2X$ (X = OMe, OC(O)R), do not undergo CO insertion even at 100°C and 1000 psi CO pressure. The facile CO insertion reaction of the ruthenium-methylene complex was rationalized with a relatively large Ru–C–Ru angle (123°), which is larger than that of the sp^3 hybrid orbital (109.5°). The methylene-bridged complex containing a metal–metal bond, $[Cp(CO)Ru]_2(\mu$-$CO)(\mu$-$CH_2)$, whose $Ru{-}CH_2{-}Ru$ bond angle is 81.3°, does not undergo CO insertion. These results suggest that in addition to electronic and steric effects, the bond angle of M–C–M may also have some effect on the rate of CO insertion reactions.

Most of the M–C–Si angles of complexes containing $CH_2Si(CH_3)_3$ groups are larger than that of the sp^3 hybrid orbital as listed in Table 1. The average of these angles is about $120 \pm 5°$. These complexes contain no CO group and thus are inadequate for studying CO insertion reactions. It is our interest here to synthesize

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TABLE 1. M–C–Si angles for some selected compounds

Compound	Angle (°)	Ref.
$CpRu(CO)_2CH_2SiMe_3$	119.6	This work
$Nb_2(CSiMe)_3(CH_2SiMe_3)$	119.8	4
$Mo_2(CH_2SiMe_3)_6$	121.1	5
$Cr_2(CH_2SiMe_3)_4(PMe_3)_2$	119.5	6
$W_2(CH_2SiMe_3)_6$	120	7
$Th(\eta^5\text{-}(CH_3)_5C_5)_2(CH_2SiMe_3)_2$	140	8
$In(CH_2CMe_3)(CH_2SiMe_3)$	125.1	9

complexes containing both the trimethylsilylmethyl and CO groups to find the effect of the M–C–Si angle on the rate of CO insertion. We report here the syntheses and CO insertion reactions of three metal-carbonyl complexes containing M-CH_2SiMe_3 groups (M = Ru, W, Re).

2. Experimental section

2.1. General procedure

All manipulations were carried out under an atmosphere of dry oxygen-free nitrogen by Schlenk techniques or in a nitrogen-filled glovebox, unless otherwise noted. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. THF was purified by distillation from sodium/benzophenone, and n-hexane from calcium hydride. Infrared spectra were recorded on a Perkin-Elmer 983 or Jasco IR-810 spectrometer, using cells equipped with calcium fluoride windows. NMR spectra were recorded on a Bruker AM-300WB FT-NMR spectrometer. Elemental analyses were performed with a Perkin-Elmer 240C elemental analyzer. Mass spectra were obtained on a JEOL JMS D300 spectrometer.

2.2. Starting materials

$Cp(CO)_2RuCl$ [10], $Cp(CO)_3WCl$ [11] and $NaRe(CO)_5$ [12] were prepared according to previously reported procedures. Dirhenium decacarbonyl (Strem), iodomethyltrimethylsilane (Aldrich), trimethylphosphine and triphenylphosphine (Merck) were purchased and used without further purification.

2.3. Synthesis of $Cp(CO)_2RuCH_2SiMe_3$

A solution of $ClCH_2SiMe_3$ (0.65 ml, 5.3 mmol) in diethyl ether (3 ml) was added dropwise to a three necked flask containing Mg ribbon (0.14 g, 5.8 mmol) and diethylether (3 ml). Two drops of bromoethane were added to promote this reaction. This Grignard reagent was then cooled to −5°C and added dropwise to a flask containing $Cp(CO)_2RuCl$ (0.5 g, 1.9 mmol) and diethyl ether (15 ml) at −5°C. The mixture was stirred for 4 h and allowed to warm to room temperature. Solvent was then removed under reduced pressure. The product was extracted by hexane and purified by passing through a silica gel-packed column. Yield: 0.35 g (70%). Calcd for $C_{11}H_{16}O_2RuSi$: C, 42.53; H, 5.18. Found: C, 42.71; H 5.09%. IR: ν(CO) 2015, 1965 cm^{-1}. ^1H NMR (C_6D_6): 4.51 (s, 5H, Cp), 0.05 (s, 9H, Me_3), −0.15 (s, 2H, CH_2).

2.4. Synthesis of $CpW(CO)_3CH_3SiMe_3$

The procedure was similar to that for the Ru analogue. Instead of $Cp(CO)_2RuCl$, $Cp(CO)_3WCl$ (0.59 g, 1.6 mmol) was added to the Grignard reagent to give $Cp(CO)_3WCH_2SiMe_3$. Yield: 0.2 g (35%). IR: ν(CO) 2020 cm^{-1}, 1930 cm^{-1}. ^1H NMR (C_6D_6): 4.47 (s, 5H, Cp), 0.25 (s, 9H, CH_3), −0.15 (s, 2H, CH_2). ^{13}C (acetone-d_6): −37.39 (s, CH_2), 2.57 (s, CH_3), 92.71 (s, Cp).

2.5. Synthesis of $(CO)_5ReCH_2SiMe_3$

A THF solution of $NaRe(CO)_5$ (about 1.2 mmol), separated from excess Na/Hg, was transfered to another flask and then cooled to 0°C for 20 min. A flask containing ICH_2SiMe_3 (0.23 ml, 1.6 mmol) in THF (5 ml) was also cooled to 0°C. The iodomethyltrimethylsilane solution was added dropwise to the $NaRe(CO)_5$ solution. The mixture was allowed to warm slowly to room temperature, and stirred for another 1.5 h. The solvent was removed under reduced pressure and the solid residue was extracted with hexane (30 ml) and filtered by centrifuge. Removal of solvent under reduced pressure gave oily product. Yield: 0.24 g (76%). Calcd for $C_9H_{11}O_5ReSi$: C, 26.20; H, 2.70. Found: C, 26.05; H, 2.61%. IR (n-hexane): ν(CO), 2051w, 2044w, 2011s, 1979s. ^1H NMR (C_6D_6): −0.66 (s, 2H, CH_2), 0.12 (s, 9H, Me_3). ^{13}C NMR: 2.05 (Me_3), −28.60 (CH_2), 185.37, 180.59 (carbonyl). Mass: M^+ (413), $M^+ - CH_2$ (399), $M^+ - Si$ (368), $M^+ - SiMe_3$ (340), $M^+ - CH_2SiMe_3$ (326).

2.6. Carbonylation reaction of 1 with PPh_3

Complex **1** (0.05 g, 0.12 mmol) and PPh_3 (0.10 g, 0.38 mmol) were dissolved in CH_3CN (15 ml) and the mixture heated to reflux. The reaction was monitored by IR spectroscopy and found to be complete in 5 days. The solvent was then removed under reduced pressure and the product, **4**, was purified by passing through a silica gel-packed column. Further purification was by recrystallization from a CH_2Cl_2/hexane solution. ^1H NMR ($CDCl_3$): 7.4 (m, 15H, PPh_3), 4.96 (s, 5H, Cp), 2.05 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): 255.55 (d, J(C–P) = 11.25 Hz, COMe), 206.08 (d, J(C–P) = 18.75 Hz, terminal CO), 88.79 (s, CH_3). IR (CH_2Cl_2): ν(CO), 1925 (CO), 1601 (C=O) cm^{-1}.

2.7. Carbonylation reaction of 2 with PPh_3

1. $Cp(CO)_3WCH_2SiMe_3$ (0.20 g, 0.4 mmol) and PPh_3 (0.20 g, 0.76 mmol) were dissolved in n-hexane (5 ml), and the mixture heated to reflux for 5 h. The yellow product was purified by passing through a column and found to be $Cp(CO)_2(PPh_3)WC(O)CH_3$ (**5**). Calcd for $C_{27}H_{23}O_3WP$: C, 53.1; H, 3.79. Found: C, 52.95; H, 3.80%. This structure was verified with X-ray crystallographic analysis. 2. $Cp(CO)_3WCH_2SiMe_3$ (0.10 g, 0.2 mmol) and PPh_3 (0.10 g, 0.38 mmol) were dissolved in acetone-d_6 (0.5 ml) in a 5 mm NMR tube, and the mixture heated to 60°C. The reaction was monitored by NMR and the acyl product $Cp(CO)_2WC(O)CH_2SiMe_3$ was observed. ^{1}H NMR (acetone-d_6): −0.0126 (s, 9H, Me_3), 2.85 (s, 2H, CH_2), 5.12 (d, J(H–P) = 12.3 Hz, 5H, Cp), 7.4–7.5 ppm (m, 15H, PPh_3). ^{13}C NMR (acetone-d_6): −0.123 (s, Me), 60.79 (s, CH_2), 96.21 (s, Cp), 247.68 (C = O) ppm. IR (CH_2Cl_2): ν(CO) 1924, 1837 (CO), 1601 (C=O) cm^{-1}.

2.8. Reaction of 3 with trimethylphosphite under 1 atm of CO in C_6D_6

A 5 mm NMR tube was charged with **3** (0.19 g, 0.46 mmol), $P(OMe)_3$ (0.07 ml, 0.6 mmol) and C_6D_6 (0.4 ml). The mixture was then bubbled with CO for 15 min, capped with a septum, mixed well and placed in a 88°C oil bath for 3 days. Only the substitution product $(CO)_4(P(OMe)_3)ReCH_2SiMe_3$ was observed. ^{1}H NMR (C_6D_6): −0.4 (d, J(H–P) = 9.5 Hz, 2H, CH_2), 0.36 (s, 9H, Me_3), 3.04 (d, J(H–P) = 11.6 Hz, 9H, $P(OMe)_3$. ^{13}C NMR (C_6D_6): −28.55 (d, J(C–P) = 8.9 Hz, CH_2), 2.67 (s, Me_3), 52.17 (d, J(C–P) = 11.7 Hz, $P(OMe)_3$), 191.30, 191.06, 190.87, 190.20 (carbonyl). Attempts to purify the product by passing the crude product through a silica gel-packed column led to decomposition.

2.9. Carbonylation reaction of 3 with triphenylphosphine in CD_3CN

A 5 mm NMR tube was charged with **3** (0.14 g, 0.34 mmol), PPh_3 (0.09 g, 0.34 mmol) and CD_3CN (0.8 ml). The tube was capped with a septum, mixed thoroughly and placed in a 75°C oil bath. The reaction was completed after about 7 h. Both the acyl, **6**, and substitution, **7**, products were observed. NMR for **6**: ^{1}H NMR (CD_3CN): −0.07 (s, 9H, Me_3), 2.58 (s, 2H, CH_2). ^{13}C NMR: 2.64 (s, Me_3), 63.19 (s, CH_2), 258.22 (d, J(C–P) = 9.75 Hz, C=O). NMR for **7**: ^{1}H NMR: −0.07 (s, 9H, Me_3), −0.07 (d, J(H–P) = 7.7 Hz, 2H, CH_2). ^{13}C NMR: 2.64 (s, Me_3), −21.67 (d, J(C–P) = 6.15 Hz, CH_2).

2.10. Reaction of $Cp(CO)_2RuCH_3$ with PPh_3 in CH_3CN

$Cp(CO)_2RuCH_3$ (0.05 g, 0.21 mmol) and PPh_3 (0.10 g, 0.38 mmol) were placed in a flask containing CH_3CN (0.8 ml). The mixture was then heated to reflux for 5 days. No change was observed.

TABLE 2. Crystal data for $Cp(CO)_2RuCH_2SiMe_3$ (**1**) and $Cp(CO)_2PPh_3WC(O)CH_3$ (**5**)

	1	**5**
Formula	$C_{11}H_{16}O_2SiRu$	$C_{27}H_{23}OPW \cdot 1.5C_6H_5$
FW	309.16	693.32
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	6.933(1)	8.922(2)
b, Å	8.455(1)	13.496(2)
c, Å	12.001(1)	13.925(2)
α, deg	105.88(1)	102.94(1)
β, deg	98.41(1)	109.71(2)
γ, deg	92.55(1)	87.13(1)
V, Å^3	666.7	1537.9
d_{calc}, g cm^{-3}	1.54	1.50
Z	2	2
Cryst size, mm	0.50 × 0.40 × 0.35	0.12 × 0.2 × 0.3
μ(Mo Kα), cm^{-1}	12.18	
Instrument	Nonius CAD4	
Radiation monochromated in incident beam (λ(Mo Kα), Å)	0.71073	
Temp., °C	25°C	
Scan method	$2\theta/\omega$	
Scan width	$2(0.7 + 0.35 \tan \theta)$	
Data collcn range (2θ), deg	4–70	4–50
Tot. no. of reflctns	5860	5405
No. of unique data $I_0 > 3\sigma(I_0)$	4586	4596
No. of params refined	137	371
R_F	0.0296	0.0253
R_{Fw}	0.0254	0.019

2.11. Reaction of $(CO)_5ReCH_3$ with PPh_3 in CD_3CN

A 5 mm NMR tube was charged with $(CO)_5ReCH_3$ (0.02 g, 0.059 mmol), PPh_3 (0.05 g, 0.19 mmol) and CD_3CN (0.4 ml), capped with a septum, mixed well and then placed in a 75°C oil bath. After one day, monitored by NMR, about 1/3 of the starting material disappeared and only substitution product $(CO)_4(PPh_3)ReCH_3$ was derived. ^1H NMR: −0.54 (d, 3H, $J(H-P) = 7.2$ Hz, CH_3).

2.12. X-ray crystallography

2.12.1. $CpRu(CO)_2CH_2SiMe_3$

A colourless crystal of $Cp(CO)_2RuCH_2SiMe_3$ was mounted on the top of a glass fibre with epoxy cement. A rotational photograph indicated that the crystal diffracted well. The unit cell constants were determined from 25 reflections with 2θ in the range 27–31°. These were consistent with a triclinic system, and the space group was subsequently determined to be $P\bar{1}$.

Routine 2θ–ω data collection was used to scan the possible 5860 reflections in the range 0–70°. Three check reflections monitored throughout the data collection displayed no significant gain or loss in intensity. The structure factors were obtained after a Lorentz and polarization correction. Empirical absorption corrections based on azimuthal scans of reflections of Eulerian angle (chi) near 90° were applied to the data. Crystallographic computations were carried out on a PDP 11/23 computer using the Nonius structure determination package [13].

The ruthenium atom was located in a Patterson synthesis and the remaining atoms were found in a series of alternating difference Fourier maps and least-square refinements. Anisotropic thermal parameters were used for all the atoms except the hydrogen atoms. The final residuals of the refinement were $R = 0.0296$ and $R_w = 0.0254$.

TABLE 3. Atomic coordinates of $CpRu(CO)_2CH_2SiMe_3$

Atom	x	y	z	B_{iso}
Ru	0.05518(2)	0.12829(2)	0.30245(2)	3.35(1)
SI	0.8348(1)	0.7207(1)	0.2061(1)	3.88(3)
C1	0.8730(7)	0.9233(2)	0.3203(2)	3.4(1)
C2	0.3241(3)	−0.0037(3)	0.3363(2)	5.7(2)
C3	0.3161(3)	0.0245(4)	0.2258(2)	5.9(2)
C4	0.3356(4)	0.1963(4)	0.2452(2)	7.1(3)
C5	0.3511(3)	0.2721(3)	0.3644(2)	5.3(2)
C6	0.3443(3)	0.1479(3)	0.4208(2)	5.0(2)
C7	0.8786(3)	0.1418(3)	0.1749(6)	4.7(1)
C8	0.9130(3)	0.2597(3)	0.4055(2)	4.2(1)
C9	0.7254(5)	0.7393(3)	0.0600(2)	6.4(2)
C10	0.6581(4)	0.5837(3)	0.2502(3)	6.0(2)
C11	1.0604(4)	0.6097(3)	0.1918(2)	6.2(2)
O1	0.7736(3)	0.1550(2)	0.0950(2)	7.2(1)
O2	0.8269(3)	0.3385(2)	0.4707(2)	6.4(1)
H11	0.7275	0.9660	0.3294	4.7
H12	0.9335	0.9000	0.4302	4.7
H2	0.3155	−0.1239	0.3542	3.4
H3	0.2973	−0.0668	0.1397	4.3
H4	0.3360	0.2619	0.1792	4.7
H5	0.3650	0.4056	0.4075	4.3
H6	0.3541	0.1682	0.5148	3.6
H91	0.8601	0.7225	0.0203	8.7
H92	0.6941	0.8581	0.0433	8.7
H93	0.6290	0.6436	−0.0063	8.7
H101	0.5262	0.6443	0.2617	6.7
H102	0.7248	0.5708	0.3364	6.7
H103	0.6416	0.4704	0.1815	6.7
H111	1.0263	0.4879	0.1288	6.2
H112	1.1239	0.5926	0.2760	6.2
H113	1.1714	0.6770	0.1625	6.2

2.12.2. $Cp(CO)_2(PPh_3)WC(O)CH_3$(5)

Complex **5** was crystallized from benzene and should be kept in benzene. The crystals became an amorphous powder when removed from the solvent. Therefore, the crystal was sealed in mother liquor in a capillary tube for X-ray diffraction study. The X-ray crystallographic procedures for this compound are similar to those for **1** and the final residuals of the refinement were $R = 0.0253$ and $R_w = 0.019$.

Basic information pertaining to crystal parameters and structure refinements for both Ru and W complexes are summarized in Table 2. Tables 3 and 4 list positional parameters for $Cp(CO)_2RuCH_2SiMe_3$ and $Cp(CO)_2(PPh_3)WC(O)CH_3$, respectively.

3. Results and discussion

3.1. Syntheses and characterization of $Cp(CO)_2RuCH_2SiMe_3$(1), $Cp(CO)_3WCH_2SiMe_3$(2) and $(CO)_5ReCH_2SiMe_3$(3)

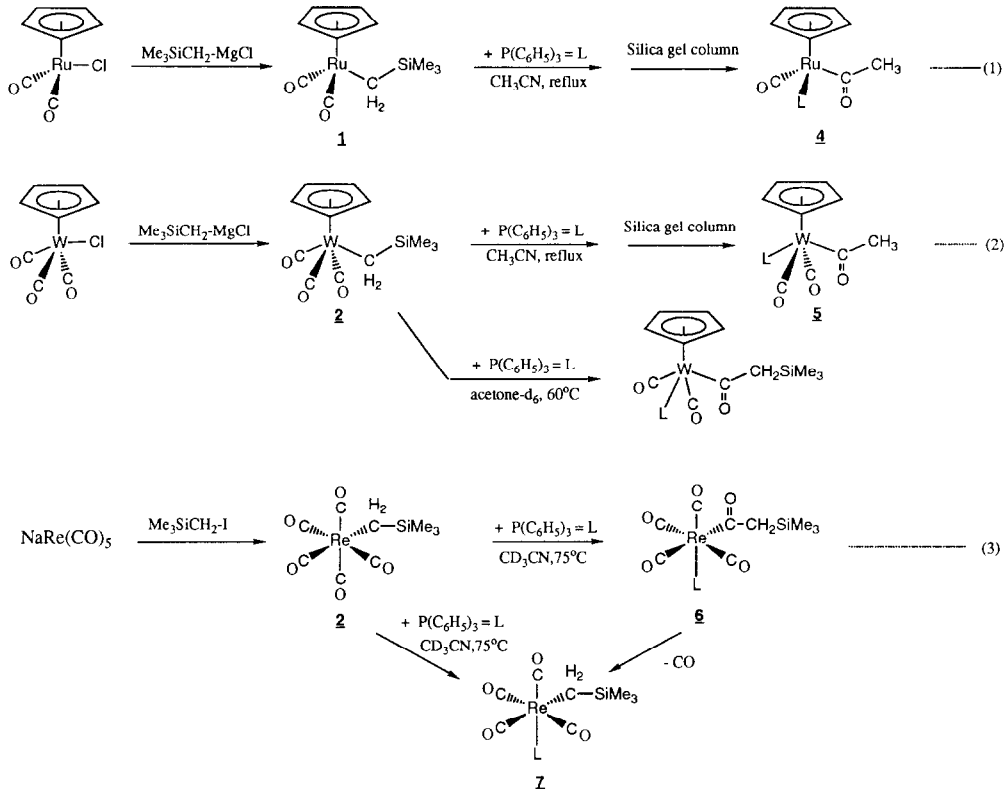
Equations (1–3) in Scheme 1 show the preparations and CO insertion reactions for complexes **1**, **2** and **3**, respectively. Complex **1** was prepared by the reaction of $Cp(CO)_2RuCl$ and $ClMgCH_2SiMe_3$ at −5°C. Complex **2** was obtained by a similar procedure, in which $Cp(CO)_3WCl$ was reacted with $ClMgCH_2SiMe_3$. Complex **1** is a stable, colourless solid. In contrast to **1**, complex **2** is an air-sensitive yellow oil. Complex **3** was prepared by adding ICH_2SiMe_3 to $Na(CO)_5Re$, which was prepared by reacting sodium amalgam with $Re_2(CO)_{10}$ in THF solvent. Complex **3** is also an air-sensitive yellow oil. All three complexes show upfield chemical shifts in the ^1H NMR spectra for the methylene hydrogen at about −0.1 ppm, indicating an electronegative character of the carbon atom at this position. The structure of **1** was characterized by X-ray crystallography. Crystals of this complex conform to the space group $P\bar{1}$ with two molecules in a unit cell.

Figure 1 shows the ORTEP drawing for **1**. Pertinent intramolecular distances and angles are listed in Table 5. It is seen from Fig. 1 that each molecule contains a η^5-cyclopentadienyl ring, two *cis*-coordinated carbon monoxide ligands and one trimethylsilylmethyl group. The two CO ligands are essentially linear. The Ru–C(7)–O(1) and Ru–C(8)–O(2) angles are 177.3(2) and 178.4(2)°, respectively. The Ru–C–Si angle is 119.6°. The structures of **2** and **3** were characterized by elemental analysis and/or spectroscopic studies.

3.2. PR_3-assisted CO insertions

Complexes **1** and **2** were treated with PPh_3 in refluxing CH_3CN and n-hexane, respectively. Products were purified by silica gel-packed column chromatography. No simple CO insertion products, such as $Cp(CO)_n(PPh_3)MC(O)CH_2SiMe_3$ (M = Ru, n = 1; M = W, n = 2) could be isolated, instead, complexes of the type $Cp(CO)_n(PPh_3)MC(O)CH_3$ (M = Ru, n = 1, **4**; M = W, n = 2, **5**) were obtained. However, in a NMR-monitored reaction of $Cp(CO)_3WCH_2SiMe_3$ with PPh_3 in acetone-d_6 at 60°C, the acyl product $Cp(CO)_2(PPh_3)WC(O)CH_2SiMe_3$ was observed. The structure of **4** was characterized by spectroscopic studies. The identity of the C=O group is supported by the observation of an IR absorption at 1601 cm^{-1}, which is known to be characteristic of the metal-coordinated acyl groups. The structure of **5** was characterized by X-ray crystallography. Crystals of **5** conform to the space group $P\bar{1}$ with two molecules in a unit cell. Figure 2 shows the ORTEP diagram for this complex. Pertinent molecular distances and angles are listed in Table 6. The structure of **5** shows that the trimethylsilylmethyl group has been transformed to methyl after insertion of CO. The bond distances W–C(7) = 2.211(7) Å, C(7)–O(3) = 1.207(5) Å and angles W–C(7)–O(3) = 122.9(3)°, W–C(7)–C(8) = 122.8(3)°, O(3)–C(7)–C(8) = 114.2(3)° are known to be characteristic of metal-coordinated acyl group. The two *trans*-coordinated carbon monoxide ligands (C(5)–W–C(6) = 106.9(1)°) are essentially linear. The W–C(5)–O(1) and W–C(6)–O(2) angles are 175.4(3)° and 175.5(3)°, respectively. The phosphine is *trans* to the acyl group with C(7)–W–P = 135.8(1)°.

The phosphine-promoted CO insertion reactions for **3** have been investigated and studied by NMR. No change was observed when **3** was reacted with trimethylphosphite in C_6D_6 at room temperature for several days. The substitution product $(CO)_4P(OMe)_3ReCH_2SiMe_3$ was obtained when the temperature was in-



Scheme 1. The pathways of preparations and CO insertions for complexes **1** (eqn. (1)), **2** (eqn. (2)) and **3** (eqn. (3)).

TABLE 4. Atomic coordinates and anisotropic thermal parameters of $Cp(CO)_2PPh_3WC(O)CH_3$

Atom	x	y	z	B_{iso}
W	0.00076(2)	0.99168(2)	0.25618(1)	3.25(1)
P	0.0745(1)	0.8124(1)	0.2264(1)	3.1(1)
O1	−0.1834(4)	0.9340(3)	0.0172(2)	5.4(2)
O2	−0.1832(1)	0.9067(3)	0.3760(2)	7.5(2)
O3	0.7718(4)	0.1652(3)	0.2669(3)	6.7(2)
C5	−0.1182(5)	0.9519(3)	0.1063(3)	4.0(2)
C6	−0.1172(5)	0.9349(4)	0.3280(3)	4.5(3)
C7	0.7759(5)	0.0745(3)	0.2356(3)	4.8(3)
C8	0.6116(6)	0.0215(4)	0.1808(4)	7.0(4)
C11	0.1363(1)	0.7601(3)	0.1127(3)	3.3(2)
C12	0.1781(5)	0.8221(3)	0.0594(3)	4.4(3)
C13	0.2249(5)	0.7803(4)	−0.0257(3)	5.5(3)
C14	0.2305(5)	0.6778(4)	−0.0584(3)	5.3(4)
C15	0.1917(5)	0.6146(4)	−0.0052(3)	4.6(3)
C16	0.1432(5)	0.6555(3)	0.0789(3)	4.1(2)
C21	0.2423(4)	0.7853(3)	0.3353(3)	3.2(2)
C22	0.3870(5)	0.7543(3)	0.3251(3)	4.1(3)
C23	0.5139(5)	0.7384(4)	0.4111(3)	4.6(3)
C24	0.4940(5)	0.7521(4)	0.5054(3)	4.6(3)
C25	0.3536(5)	0.7841(4)	0.5181(3)	4.6(3)
C26	0.2295(5)	0.8019(3)	0.4336(3)	4.0(2)
C31	−0.0835(4)	0.7217(3)	0.2093(3)	3.2(2)
C32	−0.0716(5)	0.6529(3)	0.2697(3)	4.1(2)
C33	−0.1962(5)	0.5903(4)	0.2546(3)	5.0(3)
C34	−0.3364(5)	0.5938(4)	0.1768(4)	5.3(3)
C35	−0.3512(5)	0.6593(4)	0.1137(4)	5.5(3)
C36	−0.2264(5)	0.7232(4)	0.1288(3)	5.0(3)
C41	0.1232(5)	1.1316(3)	0.3830(3)	4.6(3)
C42	0.2304(5)	1.0516(3)	0.3975(3)	4.3(3)
C43	0.2776(5)	1.0252(4)	0.3090(3)	4.8(3)
C44	0.2027(5)	1.0890(4)	0.2412(3)	4.9(3)
C45	0.1049(5)	1.1525(3)	0.2861(3)	4.6(3)
C91	−0.3872(6)	0.2974(4)	0.1760(4)	6.6(3)
C92	0.5062(6)	0.3575(4)	0.2527(4)	6.7(4)
C93	0.4707(6)	0.4485(4)	0.3038(4)	5.8(3)
C94	0.3186(6)	0.4794(4)	0.2801(4)	6.3(3)
C95	0.2007(6)	0.4183(4)	0.2037(4)	6.1(3)
C96	0.2337(6)	0.3279(4)	0.1516(4)	6.0(3)
C101	0.9472(6)	0.4023(4)	0.4523(4)	5.7(3)
C102	0.8650(5)	0.4645(4)	0.5058(4)	5.6(3)
C103	0.9167(6)	0.5624(4)	0.5532(4)	6.0(3)

creased to 80°C. Attempts to purify the product by column chromatography led to decomposition. The product was thus identified by spectroscopic method. The coupling constants $J(H-P) = 9.5$ Hz and $J(C-P) = 8.9$ Hz were obtained for the CH_2 group in the ^1H and ^{13}C NMR, respectively. The reaction of **3** with PPh_3 in benzene at 75°C gave also only the substitution product, $(CO)_4(PPh_3)ReCH_2SiMe_3$. If acetonitrile was used as a solvent, and the reaction was monitored by NMR, both the acyl complex, $(CO)_4(PPh_3)ReC(O)CH_2SiMe_3$ (**6**) and the substitution product, $(CO)_4(PPh_3)ReCH_2SiMe_3$ (**7**) were observed at 75°C. Complexes **6** and **7** were characterized by ^1H and ^{13}C NMR spectroscopic studies. When this reaction was carried

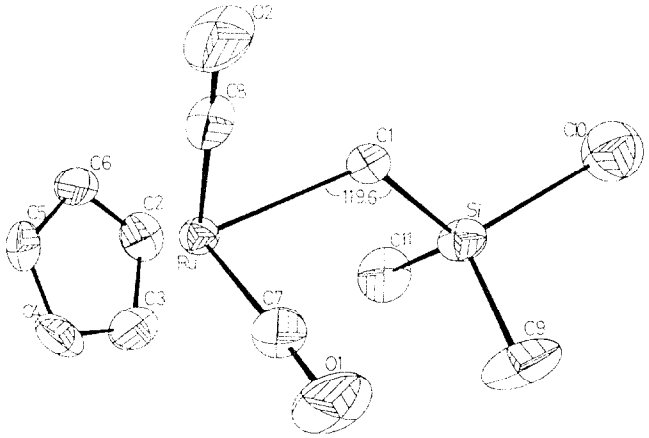


Fig. 1. ORTEP drawing of $Cp(CO)_2RuCH_2SiMe_3$.

out at room temperature no substitution or insertion product was seen. The reaction of **3** with PPh_3 in CD_3CN is shown in eqn. (3) in Scheme 1, in which the acyl complex gradually decarbonylated to become a substitution complex. The coupling constant between the acyl carbon and the phosphorus atoms of **6** and that between the methylene hydrogen and phosphorus atoms of **7** were found to be $J(C-P) = 9.7$ Hz and $J(H-P) = 7.7$ Hz, respectively, and the products are thus assigned as *cis*-isomers. These coupling constants are similar to those found for *cis*-$(CO)_4(PPh_2H)MnC(O)CH_2SiMe_3$ [15] and *cis*-$Pt(CH_2SiMe_3)_2(PMe_2Ph)_2$ [16], which were $J(C-P) = 14$ Hz, and

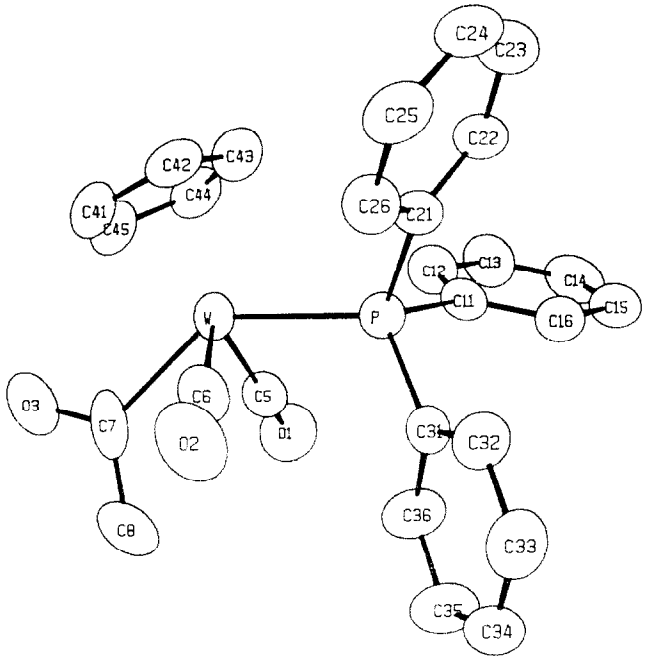


Fig. 2. ORTEP drawing of $Cp(CO)_2PPh_3WC(O)CH_3$.

TABLE 5. Selected bond distances (Å) and angles (deg) of $CpRu(CO)_2CH_2SiMe_3$

Distances					
Ru–C1	2.176(1)	Ru–C2	2.258(2)	Ru–C3	2.252(2)
Ru–C4	2.256(6)	Ru–C5	2.253(2)	Ru–C6	2.252(2)
Ru–C7	1.848(2)	Ru–C8	1.854(2)	Si–C1	1.858(1)
Si–C9	1.856(2)	Si–C10	1.877(2)	Si–C11	1.865(1)
C2–C3	1.404(3)	C2–C6	1.386(3)	C3–C4	1.403(1)
C4–C5	1.384(4)	C5–C6	1.393(3)	C7–O1	1.150(1)
C8–O2	1.140(2)				
Angles					
C1–Ru–C2	89.74(8)	C1–Ru–C3	107.60(9)		
C1–Ru–C4	143.86(9)	C1–Ru–C5	143.86(8)		
C1–Ru–C6	107.69(8)	C1–Ru–C7	90.65(8)		
C1–Ru–C8	85.01(8)	C2–Ru–C3	36.26(9)		
C2–Ru–C4	59.94(9)	C2–Ru–C5	60.07(9)		
C2–Ru–C6	35.80(9)	C2–Ru–C7	137.8(1)		
C2–Ru–C8	130.89(9)	C3–Ru–C4	36.3(1)		
C3–Ru–C5	60.40(9)	C3–Ru–C6	60.26(9)		
C3–Ru–C7	104.8(1)	C3–Ru–C8	159.28(9)		
C4–Ru–C5	35.7(1)	C4–Ru–C6	59.78(8)		
C4–Ru–C7	99.19(9)	C4–Ru–C8	129.0(1)		
C5–Ru–C6	36.17(9)	C5–Ru–C7	124.78(9)		
C5–Ru–C8	99.67(9)	C6–Ru–C7	158.86(9)		
C6–Ru–C8	100.67(9)	C7–Ru–C8	91.1(1)		
C1–Si–C9	112.1(1)	C1–Si–C10	107.8(1)		
C1–Si–C11	114.0(1)	C9–Si–C10	107.4(1)		
C9–Si–C11	109.2(1)	C10–Si–C11	105.9(1)		
Ru–C1–Si	121.3(1)	Ru–C2–C3	71.7(1)		
Ru–C2–C6	71.9(1)	C3–C2–C6	108.3(2)		
Ru–C3–C2	72.1(1)	Ru–C3–C4	72.0(1)		
C2–C3–C4	106.9(2)	Ru–C4–C3	71.7(1)		
Ru–C4–C5	72.0(1)	C3–C4–C5	108.8(2)		
Ru–C5–C4	72.2(1)	Ru–C5–C6	71.8(1)		
C4–C5–C6	107.7(2)	Ru–C6–C2	72.3(1)		
Ru–C6–C5	72.0(1)	C2–C6–C5	108.3(2)		
Ru–C7–O1	177.3(2)	Ru–C8–O2	178.4(2)		

J(H–P) = 7.8 Hz, respectively. The *trans*-isomer has, in general, larger coupling constants, *e.g.*, J(H–P) = 19.5 Hz for *trans*-$PtH(CH_2SiMe_3)(PEt_3)_3$ [16].

TABLE 6. Selected bond distances (Å) and angles for $Cp(CO)_2PPh_3WC(O)CH_3$

Distances			
W–P	2.457(1)	W–C5	1.958(3)
W–C6	1.957(4)	W–C7	2.211(4)
P–C11	1.832(3)	P–C21	1.827(3)
P–C31	1.832(3)	O1–C5	1.153(4)
O2–C6	1.157(5)	O3–C7	1.207(5)
C7–C8	1.533(7)		
Angles			
P–W–C5	81.5(1)	P–W–C6	78.6(1)
P–W–C7	135.8(1)	C5–W–C6	106.9(1)
C5–W–C7	75.4(1)	C6–W–C7	73.0(1)
W–P–C11	118.5(1)	W–P–C21	112.4(1)
W–P–C31	114.6(1)	W–C5–O1	175.4(3)
W–C6–O2	175.5(3)	W–C7–O3	122.9(3)
W–C7–C8	122.8(3)	O3–C7–C8	114.2(3)

The reactions that lead to the formation of **4** and of **5** are notable in that the C–Si bonds were cleaved. Such a C–Si bond cleavage has been found in the reaction between $[Cp(CO)_3Mo]^-Na^+$ and Me_3SiCH_2I in THF which gave $Cp(CO)_3Mo$–Me as the principal product and only a trace (5%) of $Cp(CO)_3Mo$–CH_2SiMe_3 [17]. The formation of $Cp(CO)_3Mo$–Me was shown to proceed via attack of $[Cp(CO)_3Mo]^-$ upon $Cp(CO)_3Mo$–CH_2SiMe_3. The effect of transition metal in making labile the C–Si bond was attributed to the stability of $Cp(CO)_3Mo$–CH_2^-. However, reagents like $Cp(CO)_2Ru^-$ and $Cp(CO)_3W^-$ do not exist in present reaction systems. In the CO insertion reaction of $Cp(CO)_2FeCH_2SiMe_3$ [18] using triphenylphosphine as the entering ligand, both CO insertion product, $Cp(CO)(PPh_3)FeC(O)CH_2SiMe_3$, and phosphine substituted product, $Cp(CO)(PPh_3)FeCH_2SiMe_3$, were obtained. The reaction between $Cp(CO)(PPh_3)Fe$-$C(O)CH_2SiMe_3$ and HCl has been found to give $Cp(CO)(PPh_3)FeC(O)Me$ [18]. It is thus possible that the formation of **4** or **5** is due to the acid in silica gel

during separation. Indeed, in a NMR monitored reaction of **2** with PPh_3 the major product observed was the insertion one.

CO insertion reactions of $Cp(CO)_2RuCH_3$, and $Cp(CO)_3WCH_3$ are relatively difficult. The reaction of $Cp(CO)_2RuCH_3$ with PPh_3 in refluxing acetonitrile for 5 days gave no expected acyl product. It was reported that the reaction of $Cp(CO)_3WCH_3$ with PPh_3 under the same reaction gave carbonylation product with only very low yield (5.7%) [14]. Contrary to the carbonylation reactions of these methyl complexes, **1** and **2** underwent phosphine promoted CO insertion reactions under relatively mild conditions. CO insertion reaction is also known to be difficult for alkyl derivatives of Re [19]. It was reported that no insertion was observed for $(CO)_5ReCH_3$ even under 320 atm of CO and at 140°C. In the reaction of $(CO)_5ReCH_3$ with PPh_3 in CD_3CN at 75°C, monitored by NMR, only the substituted product $(CO)_4PPh_3ReCH_3$ was derived. In contrast to $Cp(CO)_2RuMe$, complexes like $Cp(CO)(PPh_3)$-FeC(O)Me and $(MeC_5H_4)(CO)(PPh_3)FeC(O)Me$ were prepared easily by refluxing $Cp(CO)_2FeMe$ and $(MeC_5H_4)(CO)_2FeMe$, respectively, with excess PPh_3 in acetonitrile [20]. It is evident that the Ru–C bond is stronger than the corresponding Fe–C bond.

Some of the M–C–Si bond angles are listed in Table 1. Similar to the corresponding angle of these complexes, the Ru–C–Si bond angle of **1** is 119°. Since both **2** and **3** are oily yellow liquids at room temperature, the M–C–Si bond angle is unlikely to be obtained by X-ray crystallographic study. On the basis of those data listed in Table 1, it is reasonable to assume that the bond angles Re–C–Si and W–C–Si are about $120 \pm 5°$. These M–C–Si bond angles are greater than expected for sp^3 hybrid orbital (109.5°). Bent's rule [21] states that more electronegative substituents prefer hybrid orbitals having less s character and more electropositive substituents prefer hybrid orbitals with more s character. The effect of the relatively electropositive Ru and Si atoms in **1**, as well as of W and Si in **2** and of Re and Si in **3**, on the methylene carbon atom cause these complexes to exhibit the same structure characters (larger M–C–Si angle) as those listed in Table 1. Electronegativities of Si, Ru, W and Mo are 1.74, 1.42, 1.40 and 1.30, respectively [22]. The larger Ru–C–Ru angle (123°), compared with that of Ru–C–Si (119°), is consistent with the more electropositive character of the Ru atom.

The rate of CO insertion reaction for a metal ethyl complex is known to be faster generally than that of the corresponding methyl complex [23]. A study on the rate of CO insertion reaction for $Cp(CO)_2FeR$ in DMSO has shown the following order:

$$(Me_3Si)_2CH \gg Me_3CCH_2 > {}^{s}Bu > {}^{i}Pr > Me_3SiCH_2 > CyCH_2 > {}^{i}Bu > Et > {}^{n}Pr > Me.$$

It is clear that both the steric and electronic effects are involved and the former seem more important [23]. One thus might conclude that it is simply due to the accelerating effect of the electron-releasing group, *i.e.*, Me_3Si, which make it possible for the trimethylsilylmethyl complexes readily to undergo CO insertion reaction under mild conditions. It is noted that this electron-releasing group has resulted in a geometrical strain at the a carbon atom. The role of this strain in accelerating the CO insertion reaction is currently under investigation.

4. Supplementary materials available

Full tables of bond distances, bond angles and anisotropic thermal parameters (5 pages); and two listings of observed and calculated structure factors (74 pages) are available from the authors.

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