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Insertion of carbon monoxide into an aldehyde C=O double bond induced by an (η^3-α-silabenzyl)carbonylmolybdenum complex†

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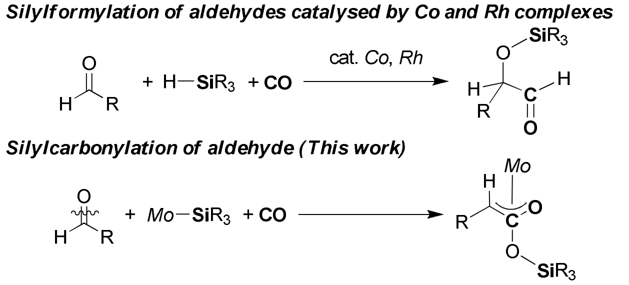
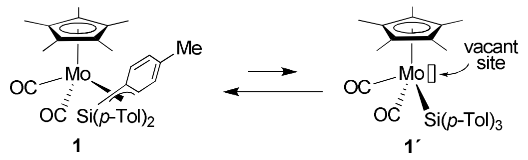
Unusual silylcarbonylation of aldehyde through CO insertion into a C=O double bond induced by a metal–silicon complex has been discovered: Treatment of an (η^3-α-silabenzyl)carbonylmolybdenum complex with alkylaldehydes afforded isolable *O*-silylated Mo–C–O three-membered-ring complexes, and one of them was subsequently converted to an η^3-oxaallyl complex at room temperature through CO insertion into the metallacycle C–O bond and incorporation of a CO molecule.

Carbon monoxide is a simple and widely-used C1 building block for production of organic compounds such as hydroformylation of unsaturated organic molecules catalysed by transition-metal complexes.[1] As a catalytic transformation reaction involving incorporation of not only a CO molecule but also a silyl group into organic molecules, Murai et al. have developed silylformylation of aldehydes catalysed by a $Co_2(CO)_8/PPh_3$ mixture where aldehydes react with tertiary silane and CO to give α-(siloxy)aldehydes (Scheme 1).[2] Wright et al. then found that some rhodium complexes are also catalytically active for the silylformylation.[3] A reasonable mechanism for these catalytic reactions involves CO insertion into an M–C(OSiR$_3$) (M = Co or Rh) bond of an α-(siloxy)alkyl complex, which is formed by migratory insertion of an aldehyde C=O double bond into an M–SiR$_3$ bond of a silyl-complex intermediate.[2,3] In this study, we discovered a new stoichiometric silylcarbonylation reaction of aldehyde induced by a metal–silicon complex, which proceeds through insertion of a CO molecule into an aldehyde C=O double bond (Scheme 1).



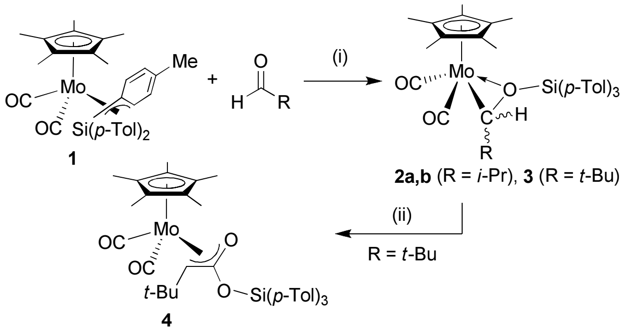
Scheme 1 Illustrations of catalytic silylformylation of aldehydes (top)[2,3] and silylcarbonylation of aldehyde via CO insertion into a C=O double bond developed in this work (bottom).

We are investigating the synthesis and reactivity of an (η^3-α-silabenzyl)carbonylmolybdenum complex Cp*Mo(CO)$_2${η^3(*Si,C,C*)-Si(*p*-Tol)$_3$} (**1**; Cp* = η^5-C_5Me_5, *p*-Tol = *p*-C_6H_4Me) bearing a unique η^3-coordination of silicon and two aromatic carbons to molybdenum.[4] Since the coordinated arene moiety of **1** is labile, complex **1** serves as a synthetic equivalent of a reactive, coordinatively unsaturated silyl complex Cp*Mo(CO)$_2${Si(*p*-Tol)$_3$} (**1′**) (Scheme 2).[4]



Scheme 2 Complex **1** as a synthetic equivalent of coordinatively unsaturated complex **1′**.

This time, we examined the reactions of **1** with alkylaldehydes. Complex **1** reacted with RCHO (R = *i*-Pr and *t*-Bu) quickly at room temperature in toluene to give Mo–C–O three-membered-ring complexes Cp*Mo(CO)$_2${η^2(*C,O*)-CH(R)OSi(*p*-Tol)$_3$} (**2**: R = *i*-Pr and **3**: R = *t*-Bu) in 83% and 76% yields, respectively (Scheme 3). Complex **2** was obtained as a mixture of two diastereomers **2a** (major) and **2b** (minor) in a 5:1 molar ratio (determined by ^{1}H NMR spectroscopy in CD_2Cl_2 at –33 °C),[5] whereas complex **3** was obtained as a single diastereomer. Although a few *O*-silylated M–C–O three-membered-ring complexes have previously been reported,[6] **2** and **3** are the first examples of this type of complex synthesised by reactions of metal–silicon complexes with carbonyl compounds.



Scheme 3 Synthesis of Mo–C–O three-membered-ring complexes **2**,**3** and conversion of **3** to η^3-oxaallyl complex **4**. *Conditions*: (*i*) toluene, r.t., 1 min. (*ii*) toluene, r.t., 5 h.

Recrystallization of a mixture of **2a** and **2b** from hexane at –35 °C afforded an orange single crystal involving only **2a**. The X-ray crystal structure analysis of **2a** revealed the existence of a Mo–C–O three-membered ring on which the *i*-Pr group is *anti* to the Cp* ligand (Fig. 1).‡ The Mo(1)–C(3) and Mo(1)–O(1) distances [2.167(6) and 2.175(4) Å, respectively][7] support the η^2-coordination of the siloxymethyl ligand.[8]

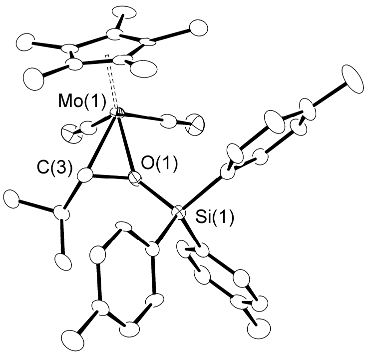
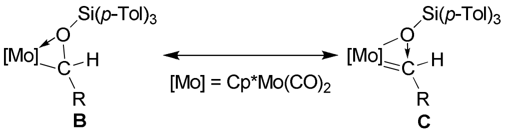


Fig. 1 Crystal structure of **2a**. One of the two independent molecules **2a**-A and **2a**-B in the asymmetric unit, i.e., molecule **2a**-A, is depicted. Selected interatomic distances (Å) and angles (°): Mo(1)–O(1) 2.175(4), Mo(1)–C(3) 2.167(6), O(1)–C(3) 1.434(7), O(1)–Mo(1)–C(3) 38.56(19).[7]

Each of the ^{1}H NMR spectra of **2a**, **2b** and **3** in C_6D_6 at room temperature shows a doublet (for **2a,b**) or a singlet (for **3**) signal assignable to the methine proton on the metallacycle carbon at δ 3.49, 4.12 and 3.94, respectively. These chemical shifts are close to those of the corresponding signals for related *O*-alkylated Mo–C–O three-membered-ring complexes (η^5-C_5H_4R')Mo(CO)$_2${η^2(*C,O*)-*cyclo*-CH(CH$_2$)$_3$O} (**A**) [δ 4.22 (R′ = H) and 4.05 (R′ = Me)].[8b] In the $^{13}C\{^1H\}$ NMR spectra of **2a** and **3** in CD_2Cl_2 at –33 °C, a signal assignable to the metallacycle carbon appears at δ 87.5 (**2a**) and 93.8 (**3**). These signals are shifted downfield in comparison with that of the methine carbon of the α-siloxyalkyl ligand in CpMo(CO)$_2$(PPh$_3$){CH(OSiHPh$_2$)(CH$_3$)} (δ 69.24)[9] and those of the corresponding carbons for metallacycles **A** [δ 75.6 (R′ = H) and 77.6 (R′ = Me)].[8b] This implies that the metallacycle carbons in **2** and **3** have some carbene character as drawn in Scheme 4 by a resonance between two canonical forms, i.e., alkyl(silylether) form **B** and carbene(siloxy) form **C**.



Scheme 4 Two possible canonical forms of Mo–C–O three-membered-ring complexes **2** (R = *i*-Pr) and **3** (R = *t*-Bu).

To determine the stereochemistry of diastereomers **2a** and **2b**, the ^{1}H-^{1}H NOESY spectrum of the mixture was measured at –33 ºC. The major isomer **2a** shows a pair of NOE cross peaks between the ^{1}H signals of the metallacycle C–H (δ 3.16) and Cp* (δ 1.65), indicating that these protons are spatially close to each other. Thus, the *i*-Pr group on the metallacycle carbon in **2a** is *anti* to the Cp* ligand, and this arrangement agrees with that of the molecule in the crystal (Fig. 1). The NOESY spectrum of **3** at –33 ºC exhibits a pair of strong cross peaks between the metallacycle C–H (δ 3.62) and the Cp* (δ 1.60) signals together with weak cross peaks between the *t*-Bu (δ 0.71) and the Cp* signals. This implies that the geometric arrangement of substituents on the metallacycle of **3** is the same as that of **2a**.

Complexes **2** and **3** are thermally unstable both in solution and in the solid state at room temperature. Although products of the thermal conversion of **2** were not characterised, the main product of that of **3** was isolated and structurally determined. When the reaction of **1** with 2,2-dimethylpropanal was performed at room temperature for a longer period (5 h), the colour of the solution initially changed from dark purple of **1** to orange of **3**, and then gradually changed to dark-red of **4**. A siloxy-substituted η^3-oxaallyl complex Cp*Mo(CO)$_2$[η^3(*O,C,C*)-OC{OSi(*p*-Tol)$_3$}CH(*t*-Bu)] (**4**) was isolated as reddish purple crystals from the reaction mixture in 40% yield (Scheme 3).[10] The yield of **4** was improved to 75% NMR yield when the same reaction was carried out under CO atmosphere (1 atm) in C_6D_6 (see ESI† for details). This result as well as the structure of **4** clearly indicates that one molecule of CO is incorporated to **3** either from another molecule of **3** or by the reaction with free CO to form **4**. The NMR-tube reaction of isolated **3** in C_6D_6 at room temperature also afforded complex **4** in 41% NMR yield, which confirms that **3** is an intermediate for the formation of **4** (see ESI†).

Single crystal X-ray analysis revealed that **4** adopts a four-legged piano-stool geometry composed of η^5-C_5Me_5, two carbonyl and η^3-oxaallyl ligands (Fig. 2).‡ The Mo(1)–O(3), Mo(1)–C(3) and Mo(1)–C(4) distances (2.186(4), 2.396(5) and 2.343(6) Å, respectively)[7] for the oxaallyl ligand clearly indicate its η^3-coordination.[11] The O(3)–C(3) and C(3)–C(4) distances (1.284(7) and 1.403(9) Å, respectively)[7] are also close to the corresponding distances (1.302(4) and 1.435(5) Å, respectively) for an (η^3-oxaallyl)tungsten complex CpW(CO)$_2${η^3(*O,C,C*)-OC(NEt$_2$)CH$_2$}.[11a]

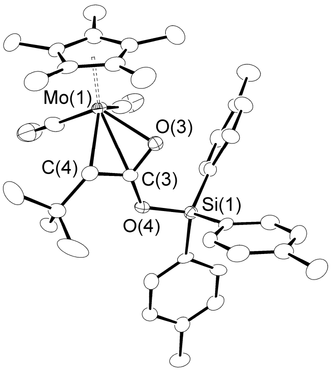
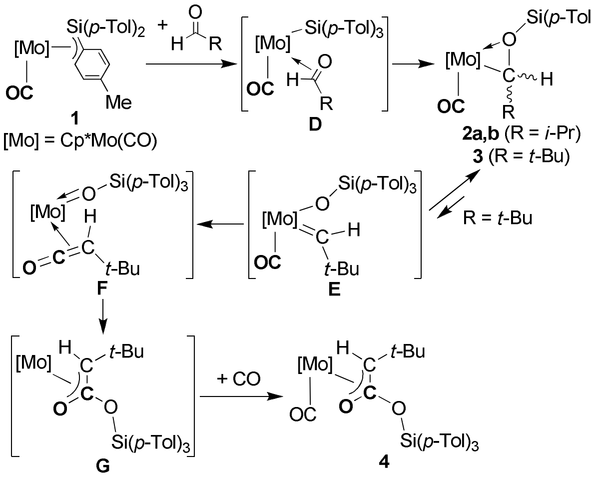


Fig. 2 Crystal structure of **4**. One of the two independent molecules **4**-A and **4**-B in the asymmetric unit, i.e., molecule **4**-A, is depicted. Selected interatomic distances (Å) and angles (º): Mo(1)–O(3) 2.186(4), Mo(1)–C(3) 2.396(5), Mo(1)–C(4) 2.343(6), O(3)–C(3) 1.284(7), O(4)–C(3) 1.355(7), C(3)–C(4) 1.403(9), O(3)–Mo(1)–C(4) 61.27(18).[7]

The ^{1}H NMR spectrum of **4** shows a signal for the methine proton of the oxaallyl ligand at δ 2.30. This chemical shift is in the range of those for η^3-oxaallyl complexes of molybdenum and tungsten (δ 1.72–3.72).[11a] In the $^{13}C\{^1H\}$ NMR spectrum of **4**, signals assignable to the central and terminal carbons of the oxaallyl ligand appear at δ 155.0 and 63.7, respectively.[11] These observations also support the structure of **4** bearing an η^3-oxaallyl ligand.

A possible mechanism for the reaction of **1** with alkylaldehydes leading to complexes **2**,**3** and subsequent conversion of **3** to complex **4** is illustrated in Scheme 5. Dissociation of the coordinated aryl carbons in **1** to generate **1′** (see Scheme 2) followed by η^2-coordination of an aldehyde molecule to molybdenum gives silyl complex **D**. The silyl ligand in **D** then migrates to the oxygen of the aldehyde to yield complexes **2** and **3**. In the case of **3**, the metallacycle C–O bond is cleaved to generate carbene(siloxy) complex **E**. A closely related cleavage of a carbon–sulfur bond in *S*-silylated Fe–C–S three-membered-ring intermediates has recently been proposed by Nakazawa et al. in the reduction of thioamides with hydrosilanes catalysed by an iron complex $CpFe(CO)_2Me$.[12] The carbene ligand then couples with a CO ligand in **E** to produce an η^2-ketene complex **F**.[13] Finally, migration of the siloxy ligand in **F** to the carbonyl carbon of the ketene ligand (forming **G**) followed by incorporation of CO as a ligand gives complex **4**. By this reaction mechanism, a CO molecule is inserted into an aldehyde C=O double bond.



Scheme 5 A possible formation mechanism of Mo–C–O three-membered-ring complexes **2**,**3** and η^3-oxaallyl complex **4**

In summary, stoichiometric silylcarbonylation of aldehyde induced by (η^3-α-silabenzyl)carbonylmolybdenum complex **1** gave η^3-oxaallyl complex **4** via an *O*-silylated Mo–C–O three-membered-ring intermediate **3**. This result implies that metal–silicon complex **1** is potentially useful as a reagent transforming carbonyl compounds through cleavage of their C=O double bonds.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details on synthesis and characterisation of **2**–**4**. CCDC reference numbers 990556 (**2a**) and 990557 (**4**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

‡ *Crystallographic data* for **2a**: $C_{37}H_{44}O_3SiMo$, M = 660.75, triclinic, space group $P1$ (no. 2), a = 8.6566(3), b = 10.9696(4), c = 35.7255(11) Å, α = 95.4889(13), β = 92.2032(14), γ = 97.1362(15)°, V = 3346.4(2) Å^3, Z = 4, T = 90 K, μ(Cu–Kα) = 3.806 mm^{-1}, 31297 reflections were measured, 11121 unique (R_{int} = 0.0239), $R1$ = 0.0740 and $wR2$ = 0.1674 (all data). We could not obtain a sufficient amount of reflections for **2a**: Data completeness to 2θ = 139.42° is 88.0%. This is caused by the gradual degradation of crystallinity of the sample under X-ray irradiation. **4**: $C_{39}H_{46}O_4SiMo$, M = 702.79, monoclinic, space group $P2_1$ (no. 4), a = 12.8069(3), b = 13.1036(4), c = 21.5568(7) Å, β = 90.7174(4)°, V = 3617.30(18) Å^3, Z = 4, T = 150 K, μ(Mo–Kα) = 0.433 mm^{-1}, 51709 reflections were measured, 15836 unique (R_{int} = 0.1025), $R1$ = 0.0853 and $wR2$ = 0.1364 (all data).

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