Reactions of quadruply chelated silyl– and germyl–molybdenum hydrido complexes with carboxylic acids and carbon dioxide: a first example of carbon dioxide fixation utilizing the *trans* effect of a silyl ligand

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Received (in Cambridge, UK) 30th August 2001, Accepted 7th November 2001 First published as an Advance Article on the web 4th December 2001

The reaction of molybdenum complexes [Mo- H_3 {E(Ph)[Ph_2PCH_2CH_2P(Ph)C_6H_4-o]_2}] (E = Si or Ge) with carboxylic acids gave carboxylato complexes where the carboxylato ligand coordinates to the metal in a unidentate mode; the formato complex was found to be an effective catalyst for carbon dioxide fixation.

Since the first preparation of the transition-metal silvl derivative, $CpFe(CO)_2SiMe_3$ (Cp = $\eta^5-C_5H_5$), by Wilkinson and coworkers in 1956,¹ numerous relevant examples have been reported.² We previously reported the unexpected formation of [MoH₃{Si(Ph)novel molybdenum-silyl complex, а $[Ph_2PCH_2CH_2P(Ph)C_6H_4-o]_2]$ **1a**, which is obtained by the reaction $[MoH_4(dppe)_2]$ thermal of 2. (dppe Ph₂PCH₂CH₂PPh₂) with PhSiH₃ and possesses an unusual quadruply chelated ligand.³ Recently this methodology has been extended to the reaction of 2 with PhGeH₃, which is a higher homologue of PhSiH₃, and have obtained the same type of complex 1b having a Mo-Ge bond.⁴ Complexes in which two metal atoms of very different character are held in close proximity seem to offer fascinating opportunities to achieve novel types of reaction. We have studied the reactivity of these complexes and a series of new complexes with this quinquidentate ligand has been synthesized from 1. For example, 1a reacted with a dialkyl malonate or gaseous dioxygen to afford an η^1 -O-enolato type complex or a peroxo type η^2 -O₂ complex 3, respectively.^{5,6} Herein we report the synthesis and some reactions of dihydrido(carboxylato)molybdenum complexes.

Treatment of **1** with two equiv. of carboxylic acids such as formic acid, acetic acid or benzoic acid in THF at room temperature readily led to the formation of monocarboxylato molybdenum complexes (**4**, E = Si; **5**, E = Ge) in good yields (70–90%, Scheme 1).† In these reactions, the evolution of hydrogen gas was qualitatively confirmed by GLC analysis. In the ¹H NMR spectra of the complexes **4**, hydrido signals appeared at around δ –7.9 as a triplet of triplets corresponding



Scheme 1

to an A₂K₂X spin system. The ³¹P{H} NMR spectra of complexes **4** contain two resonances at around δ 87 (br d, J_{PP} 122 Hz) and 58 (br d, J_{PP} 122 Hz) in a 1:1 ratio. The presence of only two resonances indicates that the molecule **4** has an effective mirror plane which contains the Mo–Si bond. The IR spectra of complexes **4** showed v(Mo–H) at 1816–1819 cm⁻¹ and two v(OCO) stretching vibrations (asym and sym) at 1609–1618 cm⁻¹ and 1326–1360 cm⁻¹, respectively. The fairly large values of $\Delta v [v(OCO)_{asym} - v(OCO)_{sym}]$ ranging from 248 to 272 cm⁻¹ suggest that the carboxylato ligands in the complexes coordinate to the metal in a unidentate fashion as shown in Scheme 1.⁷ The molybdenum–germyl complexes **5** have very similar IR and NMR spectra to **4**, implying that **4** and **5** are isostructural.

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The basic features of the structure of these complexes deduced from the spectra were fully confirmed by single crystal X-ray diffraction on **4b**. A view of the molecule is shown in Fig. 1 with selected bond distances and angles.⁸ As expected from the IR and NMR results, this complex contains a quinquidentate P_2SiP_2 ligand and a unidentate acetato ligand occupying the axial site. The structure can be compared with that of the abovementioned peroxo complex, [MoH{Si(Ph)[Ph_2-PCH_2CH_2P(Ph)C_6H_4-o]_2}(\eta^2-O_2)] **3**.⁵ The Mo–Si distance of



Fig. 1 Thermal ellipsoid plot (30% probability level) for **4b**. Selected bond lengths (Å) and angles (°): Mo1–Si1 2.515(2), Mo1–P1 2.485(2), Mo1–P2 2.507(2), Mo1–P3 2.496(2), Mo1–P4 2.466(2), Si1–C47 1.887(7), Mo1–O1 2.174(5); P1–Mo1–P2 80.31(6), P2–Mo1–P3 96.32(6), Si1–Mo1–O1 143.7(1).

2.515(2) Å in **4b** is slightly shorter than that of 2.554(5) Å in **3**. On the other hand, the mean Mo–P distance of 2.489 Å in **4b** is a little longer than that found in **3** (2.462 Å).

The parent complex **2** is known to react with carboxylic acids or allyl carboxylates to give cationic and neutral carboxylato complexes, respectively, where the carboxylato ligand coordinates to the metal in a bidentate mode.^{9,10} The unusual unidentate coordination of acetate of **4b** may be ascribed to the stability of the P_2SiP_2 coordination.

A toluene solution of complex 1a was allowed to react under CO₂ pressure (17 atm) at room temperature and 4a was isolated in 82% yield from the reaction mixture (Scheme 2). Interestingly, 4a reverted to 1a quantitatively with accompanying evolution of one mol of $\overline{CO_2}$, when warmed in benzene. The reversible insertion reaction of CO₂ into the Mo-H bond under mild conditions is an outstanding feature exhibited by complex 1a since the parent complex 2 does not react with CO_2 at room temperature although irradiation of a benzene solution of 2 under CO2 atmosphere yielded a chelated formato-O,O' complex.¹¹ We thought that the high reactivity of **1a** is due to the strong trans-influence of the Si fragment since it has been pointed out that the R₃Si group has a strong σ -donor ability and may labilize the ligand in the position trans to it.¹² Yet, to date there have been few reports concerning the influence of silvl ligands on the reactivity of transition-metal complexes.13

Subsequently, we explored the catalytic activity of **1a** towards carbon dioxide fixation [eqn. (1)]. A toluene solution of

$$HNMe_2 \xrightarrow{CO_2/H_2, \text{ cat. 1a or 4a}}_{PhMe 110 °C} \rightarrow HCONMe_2$$
(1)

complex **1a** was allowed to react under CO_2/H_2 (25/35 atm) pressure in the presence of dimethylamine at 110 °C affording 115 equivalents of *N*,*N*-dimethylformamide with respect to the complex. In this process, formato complex **4a** was also found to be an efficient catalyst. Presumably, the first step in the catalytic cycle using **1a** may be the formation of **4a**. Neither **2** nor **1b** catalyzed this process suggesting both the Mo–Si linkage and the P₂SiP₂ girdle in **1a** play an important role.

Catalytic carbon dioxide fixation has attracted considerable interest. Most of the reported studies deal with iridium, palladium and ruthenium complexes¹⁴ and reports of catalysis



Scheme 2

using Group 6 metals are rare.¹⁵ To our knowledge, complex **1a** is the first molybdenum compound which can catalyze the transformation of carbon dioxide into dialkylformamide effectively.

This work was supported by a Grant-in-Aid for Scientific Research (B) No. 10450340 and a Grant-in-Aid for Scientific Research on Priority Areas (No. 11120217) from the Ministry of Education, Science, Sports and Culture of Japan.

Notes and references

† *Typical procedure* for the preparation of **4b**: to a solution of **1a** (0.268 g, 26.8 mmol) in dry THF (20 mL) was added acetic acid (0.03 mL) under argon. The resultant solution was stirred for 3 h at ambient temperature. After removal of the solvent under reduced pressure, the residue was washed with diethyl ether and hexane. Recrystallization from THF–hexane gave **4b** (0.255g, 90%). Complex **4b**: ¹H NMR (benzene-*d*₆, 25 °C, 270 MHz): δ –7.96 (tt, *J* 43.3, 17.2 Hz, 2H, Mo–*H*), 1.23 (s, 3H, CH₃CO) 2.0–3.0 (br m, 8H, PCH₂); ³¹P{¹H} NMR (benzene-*d*₆, 109.4 MHz): δ 87.7 (br d, *J* 122 Hz); S9.1 (br d, *J* 122 Hz); Satisfactory elemental analysis data are so far not available, possibly due to the presence of silicon in the molecule.

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- 8 *Crystal data* for **4b**: yellow prism; 0.30 × 0.10 × 0.10 mm; C₆₀H₅₆O₂P₄MoSi·C₄H₈O·H₂O, *M* = 1147.14; monoclinic, space group *P*₂₁/*c*(no. 14); *a* = 23.858(1), *b* = 12.1098(3), *c* = 19.5279(7) Å, β = 90.027(1)°, *V* = 5641.9(3) Å³, *Z* = 4; *D_c* = 1.350 g cm⁻³; Rigaku RAXIS-II imaging plate area detector; 298 K; Mo-Kα radiation (λ = 0.71069 Å); μ(Mo-Kα) = 4.15 cm⁻¹; *R* = 0.051. *R_w* = 0.080 for 5376 unique reflections [*I* > 5.00σ(*I*)]. CCDC reference number 172503. See http://www.rsc.org/suppdata/cc/b1/b107837m/ for crystallographic data in CIF or other electronic format.
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