Carbonyl abstraction reactions of Cp*Mo(PMe₃)₃H with CO₂, (CH₂O)ₙ, HCO₂H, and MeOH: the synthesis of Cp*Mo(PMe₃)₂(CO)H and the catalytic decarboxylation of formic acid

Jun Ho Shin, David G. Churchill, Gerard Parkin *

Department of Chemistry, Columbia University, Havemeyer Hall, Box 866, mail code 3115, New York, NY 10027, USA

Abstract

Cp*Mo(PMe₃)₃H undergoes carbonyl abstraction reactions with a variety of reagents, including CO_2, $(CH_2O)_n$, HCO_2H, and MeOH to yield Cp*Mo(PMe₃)₂(CO)H. The reaction between Cp*Mo(PMe₃)₃H and HCO_2H has been studied by ^{1}H-NMR spectroscopy, which indicates that the initial interaction involves protonation of the molybdenum center to give [Cp*Mo(PMe₃)₃H₂][HCO₂]; upon heating to 80 °C, however, [Cp*Mo(PMe₃)₃H₂][HCO₂] is converted to the carbonyl complex Cp*Mo(PMe₃)₂(CO)H. In the presence of excess HCO_2H, Cp*Mo(PMe₃)₂(CO)H reacts further to yield Cp*Mo(PMe₃)₂(CO)(η^1-O₂CH); the latter complex undergoes decarboxylation at 80 °C and regenerates Cp*Mo(PMe₃)₂(CO)H. Thus, Cp*Mo(PMe₃)₂(CO)H serves as a catalyst for the decomposition of HCO_2H to CO_2 and H_2. Although the formate complex Cp*Mo(PMe₃)₂(CO)(η^1-O₂CH) has not been isolated, the molecular structure of the acetate derivative Cp*Mo(PMe₃)₂(CO)(η^1-O₂CMe) has been determined by X-ray diffraction. © 2002 Published by Elsevier Science B.V.

Keywords: Synthesis; Carbonyl abstraction; Catalytic decarboxylation

1. Introduction

We have previously reported the pentamethylcyclopentadienyl molybdenum trimethylphosphine complexes Cp*Mo(PMe₃)H₅, Cp*Mo(PMe₃)₂H₃, and Cp*Mo(PMe₃)₃H, together with their use to prepare dinuclear complexes that contain sulfur bridges, e.g. [Cp*Mo(μ-SMe)₂]₂ and [Cp*Mo(μ-S)(μ-SH)]₂ [1]. In this paper, we describe further studies on Cp*Mo(PMe₃)₃H that highlight its ability to abstract CO from a variety of substrates to form Cp*Mo(PMe₃)₂(CO)H, a catalyst for decarboxylation of formic acid.

2. Results and discussion

Cp*Mo(PMe₃)₃H reacts readily with CO at 80 °C to yield the carbonyl complex Cp*Mo(PMe₃)₂(CO)H (Scheme 1). The clean synthesis of Cp*Mo(PMe₃)₂(CO)H is notable in the sense that Cp*Mo(PMe₃)₂(CO)H has been previously described in the literature, but was not obtained in pure form. Specifically, Cp*Mo(PMe₃)₂(CO)H was generated as a mixture with Cp*Mo(PMe₃)(CO)₂H upon reaction of: (i) [Cp*Mo(CO)₃(PMe₃)]⁺ with LiAlH₄; and (ii) [Cp*Mo(CO)₄]⁺ with LiAlH₄ in the presence of PMe₃ [2]. It is also important to note that the data reported previously for Cp*Mo(PMe₃)₂(CO)H differ in some significant ways from those reported here. For example: (i) the ^{31}P-NMR spectroscopic signal was reported as 19.6 ppm [2], rather than 29.8 ppm; and (ii) the ^{13}C-NMR spectroscopic signal for the carbonyl group was reported as 275.0 ppm [2], rather than 253.3 ppm [3]. Additional characterization for the Cp*Mo-

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* Corresponding author. Tel.: +1-212-8548247; fax: +1-212-9321289.

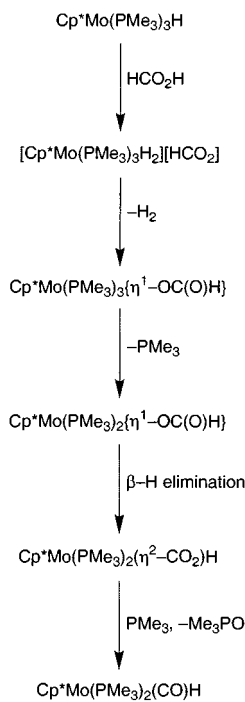*E-mail address:* parkin@chem.columbia.edu (G. Parkin).

Scheme 1.

Cp*Mo(PMe₃)₃H

$\downarrow$ CO₂, – PMe₃

Cp*Mo(PMe₃)₂(η²–CO₂)H

$\downarrow$ PMe₃, –Me₃PO

Cp*Mo(PMe₃)₂(CO)H
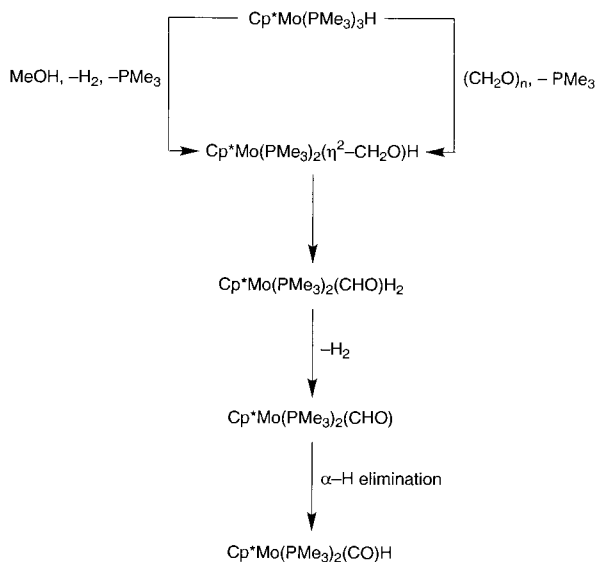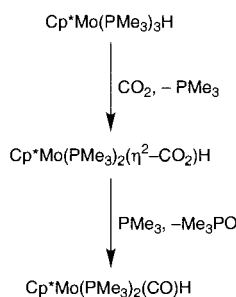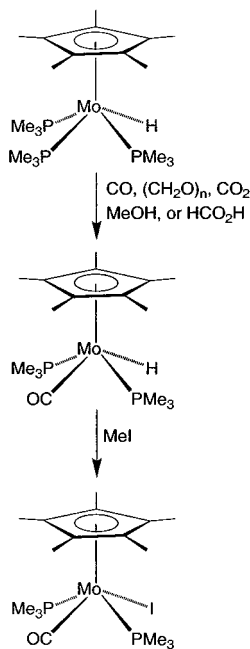
Scheme 2.

Scheme 3.

$(PMe_3)_2(CO)H$ as synthesized by reaction of $Cp^*Mo(PMe_3)_3H$ with CO is provided by the formation of the iodide derivative $Cp^*Mo(PMe_3)_2(CO)I$ upon reaction with MeI (Scheme 1).
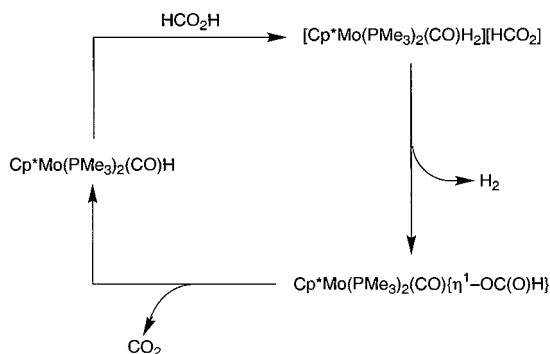
Of more interest than forming $Cp^*Mo(PMe_3)_2(CO)H$ by displacement of PMe_3 with CO, $Cp^*Mo(PMe_3)_2$-$(CO)H$ is also obtained upon reaction of $Cp^*Mo(PMe_3)_3H$ with a variety of other reagents, including, CO_2, paraformaldehyde, MeOH, and HCO_2H (Scheme 1). For the reaction between $Cp^*Mo(PMe_3)_3H$ and CO_2, ^{1}H-NMR spectroscopy demonstrates that the formation of $Cp^*Mo(PMe_3)_2(CO)H$ is accompanied by the generation of Me_3PO, which helps provide the driving force for the reaction. The formation of a carbonyl complex upon reaction with CO_2 is precedented. For example, the reaction of $Re(PMe_3)_5H$ with CO_2 yields the carbonyl complex $Re(PMe_3)_4(CO)(\eta^1$-$O_2CH)$, and the reactions of a variety of metal halides with Na in PMe_3 solvent under a CO_2 atmosphere yield carbonyl complexes, e.g. *cis*-$Cr(PMe_3)_4(CO)_2$, Mo-$(PMe_3)_5(CO)$, $W(PMe_3)_5(CO)$, and *trans*-$Fe(PMe_3)_4$-$(CO)_2$ [4]. Furthermore, η^2-CO_2 complexes are known to decompose to carbonyl derivatives. For example, $Ni(PCy_3)_2(CO_2)$ decomposes to $Ni(PCy_3)_2(CO)_2$, while $Fe(PMe_3)_4(CO_2)$ decomposes to $Fe(PMe_3)_3(CO)(CO_3)$ [5].

It is also worth noting that the formation of a carbonyl complex from CO_2 is the reverse of a common reaction that is typically used to displace CO from a metal center. Specifically, reaction of a metal carbonyl complex with R_3NO is a common means of effecting displacement of a carbonyl ligand as CO_2 [6]. It is therefore, postulated that the reaction between $Cp^*Mo(PMe_3)_3H$ and CO_2 involves initial displacement of PMe_3 and generation of a CO_2 adduct, $Cp^*Mo(PMe_3)_2(\eta^2$-$CO_2)H$, which undergoes an oxygen atom abstraction with the liberated PMe_3 to yield the carbonyl complex $Cp^*Mo(PMe_3)_2(CO)H$ (Scheme 2). The ability of PMe_3 to promote deoxygenation of CO_2 and form a metal carbonyl complex, whereas R_3NO effects the opposite reaction, is presumably a consequence of a stronger phosphine–oxide versus amine–oxide bond [7].

The reaction of $Cp^*Mo(PMe_3)_3H$ with MeOH to generate, inter alia, $Cp^*Mo(PMe_3)_2(CO)H$ is postulated to occur via a sequence involving: (i) formation of a methoxide derivative; (ii) dehydrogenation to a formaldehyde complex; (iii) conversion to a formyl-hydride derivative; (iv) reductive-elimination of H_2; and (v) α-H elimination (Scheme 3). The transformation comprises steps that are, in essence, the reverse of those required for the metal catalyzed hydrogenation of carbon monoxide and the formation of oxygenates in the Fischer–Tropsch synthesis reaction [8]. An exemplary illustration of dehydrogenation of a formaldehyde ligand [9] to a carbonyl ligand is provided by the reaction of

Cp*Mo(PMe$_3$)$_3$H

$\downarrow$ HCO$_2$H

[Cp*Mo(PMe$_3$)$_3$H$_2$][HCO$_2$]

$\downarrow$ −H$_2$

Cp*Mo(PMe$_3$)$_3${η^1−OC(O)H}

$\downarrow$ −PMe$_3$

Cp*Mo(PMe$_3$)$_2${η^1−OC(O)H}

$\downarrow$ β−H elimination

Cp*Mo(PMe$_3$)$_2$(η^2−CO$_2$)H

$\downarrow$ PMe$_3$, −Me$_3$PO

Cp*Mo(PMe$_3$)$_2$(CO)H

Scheme 4.

Cp*Mo(PMe$_3$)$_2$(CO)H

[Cp*Mo(PMe$_3$)$_2$(CO)H$_2$][HCO$_2$]

HCO$_2$H

H$_2$

Cp*Mo(PMe$_3$)$_2$(CO){η^1−OC(O)H}

CO$_2$

Scheme 5.

W(PMe$_3$)$_4$(η^2-OCH$_2$)H$_2$ with a hydrogen acceptor (e.g. propene) to give W(PMe$_3$)$_4$(CO)H$_2$ [10–12]. Furthermore, an example of α-H elimination of a formyl compound is provided by the facile conversion of Cp*Mo(PPh$_3$)(CO)$_2$(CHO) to Cp*Mo(PPh$_3$)(CO)$_2$H at −40 °C [13,14]. The formaldehyde and formyl complexes are also postulated intermediates in the formation of Cp*Mo(PMe$_3$)$_2$(CO)H upon reaction of Cp*Mo(PMe$_3$)$_3$H with paraformaldehyde (Scheme 3).

The reaction between Cp*Mo(PMe$_3$)$_3$H and HCO$_2$H has been studied by ^{1}H-NMR spectroscopy, which indicates that the initial interaction involves protonation of the molybdenum center to give [Cp*Mo(PMe$_3$)$_3$-H$_2$][HCO$_2$] (Scheme 4). The presence of two hydride ligands in [Cp*Mo(PMe$_3$)$_3$H$_2$]$^+$ is confirmed by the observation of a triplet ($J_{P-H} = 49$ Hz) in the ^{31}P{^{1}H–Me} selectively decoupled NMR spectrum.

Precedent for the formation of [Cp*Mo(PMe$_3$)$_3$H$_2$]$^+$ is provided by the observation that the analogous complexes [CpMo(PMe$_3$)$_3$H$_2$][BF$_4$] [15] and [CpW(PMe$_3$)$_3$-H$_2$][BF$_4$] [16] have been obtained by reactions of CpM(PMe$_3$)$_3$H (M = Mo, W) with HBF$_4$. Upon heating to 80 °C, however, [Cp*Mo(PMe$_3$)$_3$H$_2$][HCO$_2$] is converted to the carbonyl complex Cp*Mo(PMe$_3$)$_2$-(CO)H, accompanied by elimination of H$_2$ and Me$_3$PO. The reaction is proposed to occur via reductive elimination of H$_2$, followed by coordination of formate, to yield Cp*Mo(PMe$_3$)$_3$(η^1-O$_2$CH). Subsequent dissociation of PMe$_3$ and β-hydrogen elimination would generate the CO$_2$ complex Cp*Mo(PMe$_3$)$_2$(η^2-CO$_2$)H (Scheme 4). As suggested above, oxygen abstraction from the coordinated CO$_2$ by PMe$_3$ would generate Cp*Mo(PMe$_3$)$_2$(CO)H and Me$_3$PO.

Although Cp*Mo(PMe$_3$)$_2$(CO)H is obtained by reaction of Cp*Mo(PMe$_3$)$_3$H with one equivalent of HCO$_2$H, Cp*Mo(PMe$_3$)$_2$(CO)H reacts further with HCO$_2$H to generate an orange species that has been characterized by ^{1}H-NMR spectroscopy and mass spectrometry as Cp*Mo(PMe$_3$)$_2$(CO)(η^1-O$_2$CH). However, upon heating to 80 °C, Cp*Mo(PMe$_3$)$_2$(CO)(η^1-O$_2$CH) undergoes decarboxylation and regenerates Cp*Mo-(PMe$_3$)$_2$(CO)H [17]. Thus, Cp*Mo(PMe$_3$)$_2$(CO)H serves as a catalyst for the decomposition of HCO$_2$H to CO$_2$ and H$_2$. The catalytic decomposition of formic acid is the reverse of the commercially more important reduction of CO$_2$ to formic acid, which has been widely studied [18,19].

A proposed, simplified, catalytic cycle for the Cp*Mo(PMe$_3$)$_2$(CO)H mediated decarboxylation of formic acid is illustrated in Scheme 5. In this regard, it is worth noting that the iodide analogue Cp*Mo-
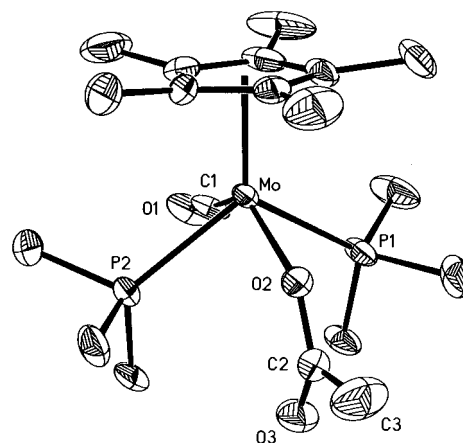
Fig. 1. Molecular Structure of Cp*Mo(PMe$_3$)$_2$(CO)(η^1-O$_2$CMe). Selected bond lengths (Å) and angles (°): Mo–C(1) 1.874(9), Mo–O(2) 2.167(4), Mo–P(1) 2.462(2), Mo–P(2) 2.454(2), C(1)–O(1) 1.200(9), C(2)–O(2) 1.277(8), C(2)–O(3) 1.212(8), C(2)–C(3) 1.504(11); C(1)–Mo–O(2)136.2(2), C(1)–Mo–P(1) 75.6(3), C(1)–Mo–P(2) 75.7(2), P(1)–Mo–P(2) 113.9(1), O(2)–Mo–P(1) 80.4(1), O(2)–Mo–P(2) 81.4(1), Mo–O(2)–C(2) 138.6(5).

(PMe$_3$)$_2$(CO)I is ineffective as a catalyst for the decomposition of HCO$_2$H, thereby clearly indicating the important role that the hydride ligand plays in the catalytic cycle. Support for the formation of Cp*Mo(PMe$_3$)$_2$(CO)(η^1-O$_2$CH) is provided by the observation that Cp*Mo(PMe$_3$)$_2$(CO)H reacts with MeCO$_2$H and EtCO$_2$H to give Cp*Mo(PMe$_3$)$_2$-(CO)(η^1-O$_2$CMe) and Cp*Mo(PMe$_3$)$_2$(CO)(η^1-O$_2$CEt), respectively, and Cp*Mo(PMe$_3$)$_2$(CO)(η^1-O$_2$CMe) has been structurally characterized by X-ray diffraction (Fig. 1). In contrast to Cp*Mo(PMe$_3$)$_2$(CO)(η^1-O$_2$CH), however, Cp*Mo(PMe$_3$)$_2$(CO)(η^1-O$_2$CMe) and Cp*-Mo(PMe$_3$)$_2$(CO)(η^1-O$_2$CEt) are stable towards elimination of CO$_2$ because β-alkyl elimination is generally less favored than β-hydrogen elimination [20,21].

3. Experimental

3.1. General considerations

All manipulations were performed using a combination of glovebox, high-vacuum or Schlenk techniques [22]. Solvents were purified and degassed by standard procedures and all commercially available reagents were used as received, unless otherwise noted in the experimental procedures. IR spectra were recorded as KBr pellets or neat samples on Perkin–Elmer 1430 or 1600 spectrophotometers and are reported in cm^{-1}. Mass spectra were obtained on a Nermag R10-10 mass spectrometer using chemical ionization (CH$_4$) techniques. Elemental analyses were measured using a Perkin–Elmer 2400 CHN Elemental Analyzer. ^{1}H-NMR spectra were recorded on Varian VXR-200 (200.057 MHz), VXR-300 (299.943 MHz), and VXR-400 (399.95 MHz) spectrometers. ^{13}C- and ^{31}P-NMR spectra were recorded on a Varian VXR-300 spectrometer. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to SiMe$_4$ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity ($\delta = 7.15$ for C$_6$D$_5$H and $\delta = 7.26$ for CHCl$_3$) and the ^{13}C resonances ($\delta = 128.0$ for C$_6$D$_6$ and $\delta = 77.0$ for CDCl$_3$), respectively. ^{31}P-NMR chemical shifts are reported in ppm relative to 85% H$_3$PO$_4$ ($\delta = 0$) and were referenced using P(OMe)$_3$ ($\delta = 141.0$) as external standard. All coupling constants are reported in Hz. Cp*Mo-(PMe$_3$)$_3$H was obtained by the literature method [1].

3.2. Synthesis of Cp*Mo(PMe$_3$)$_2$(CO)H

A solution of Cp*Mo(PMe$_3$)$_3$H (100 mg, 0.22 mmol) in C$_6$H$_6$ (10 ml) was treated with CO (1 atm) for 4 days at 80 °C. After this period, the volatile components were removed from the mixture, and the residue was dried in vacuo to give Cp*Mo(PMe$_3$)$_2$(CO)H as a brown solid (85 mg, 95%). Anal. Calc. for

C$_{17}$H$_{34}$MoOP$_2$: C, 49.5; H, 8.3. Found: C, 49.3; H, 7.9%. MS: $m/z = 414$ [M$^+$]. IR data (KBr disk, cm^{-1}): 2968 (m), 2903 (s), 1773 (vs) [ν(C≡O)], 1701 (m) [ν(Mo–H)], 1478 (w), 1422 (m), 1376 (m), 1295 (w), 1276 (m), 1027 (w), 936 (vs), 850 (w), 711 (m), 665 (m), 571 (w), 499 (w). ^{1}H-NMR (C$_6$D$_6$): − 6.85 [t, $^2J_{P-H} =$ 78, 1H, MoH], 1.31 [d, $^2J_{P-H} = 8$, 18H, 2P(CH_3)$_3$], 1.91 [s, 15H, C$_5$(CH_3)$_5$]. ^{13}C-NMR (C$_6$D$_6$): 12.5 [q, $^1J_{C-H} =$ 126, 5C, C$_5$(CH$_3$)$_5$], 25.0 [dq, $^1J_{C-H} = 127$, $^1J_{C-P} = 28$, 6C, 2 P(CH$_3$)$_3$], 100.6 [s, 5C, C_5(CH$_3$)$_5$], 253.3 [dt, $^2J_{C-P} = 29$, $^2J_{C-H} = 3$, 1C, CO]. ^{31}P{^{1}H}-NMR (C$_6$D$_6$): 29.8 [s].

3.3. Synthesis of Cp*Mo(PMe$_3$)$_2$(CO)I

A solution of Cp*Mo(PMe$_3$)$_2$(CO)H (50 mg, 0.12 mmol) in C$_6$H$_6$ (10 ml) was treated with excess CH$_3$I (350 mg, 2.47 mmol) and stirred at room temperature (r.t.) for 2 h. After this period, the volatile components were removed from the mixture, and the residue was dried in vacuo to give Cp*Mo(PMe$_3$)$_2$(CO)I as an orange solid. Anal. Calc. for C$_{17}$H$_{33}$IMoOP$_2$: C, 37.9; H, 6.2. Found: C, 37.8; H, 6.1%. MS: $m/z = 540$ [M$^+$]. IR data (KBr disk, cm^{-1}): 2965 (m), 2904 (s), 1778 (vs) [ν(C≡O)], 1477 (m), 1454 (m), 1421 (m), 1375 (s), 1297 (m), 1274 (s), 1095 (m), 1024 (s), 944 (vs), 851 (m), 802 (m), 717 (m), 665 (m), 579 (w), 559 (w), 524 (w). ^{1}H-NMR (C$_6$D$_6$): 1.48 [d, $^2J_{P-H} = 8$, 18H, 2P(CH_3)$_3$], 1.70 [s, 15H, C$_5$(CH_3)$_5$]. ^{13}C-NMR (C$_6$D$_6$): 12.1 [q, $^1J_{C-H} = 127$, 5C, C$_5$(CH$_3$)$_5$], 20.3 [dq, $^1J_{C-H} = 132$, $^1J_{C-P} = 24$, 6C, 2P(CH$_3$)$_3$], 102.1 [s, 5C, C_5(CH$_3$)$_5$], 271.0 [t, $^2J_{C-P} = 34$, 1C, CO]. ^{31}P{^{1}H}-NMR (C$_6$D$_6$): 7.2 [s].

3.4. Reaction of Cp*Mo(PMe$_3$)$_3$H with CO$_2$

A solution of Cp*Mo(PMe$_3$)$_3$H (ca. 10 mg) in C$_6$D$_6$ (1 ml) was heated at 80 °C under CO$_2$. ^{1}H-NMR spectroscopy showed the formation of Cp*Mo(CO)-(PMe$_3$)$_2$H (ca. 70%) and Me$_3$PO after 1 day.

3.5. Reaction of Cp*Mo(PMe$_3$)$_3$H with (CH$_2$O)$_n$

A mixture of Cp*Mo(PMe$_3$)$_3$H (ca. 10 mg) and paraformaldehyde (ca. 10 mg) in C$_6$D$_6$ (1 ml) was heated at 80 °C. ^{1}H-NMR spectroscopy showed the formation of Cp*Mo(PMe$_3$)$_2$(CO)H (ca. 40%) inter alia. Prolonged heating resulted in subsequent reaction of Cp*Mo(PMe$_3$)$_2$(CO)H with paraformaldehyde to form an unidentified complex.

3.6. Reaction of Cp*Mo(PMe$_3$)$_3$H with MeOH

A solution of Cp*Mo(PMe$_3$)$_3$H (ca. 10 mg) in C$_6$D$_6$ (1 ml) was treated with MeOH (ca. 10 mg) heated at

80 °C. ^{1}H-NMR spectroscopy showed the formation of Cp*Mo(PMe$_3$)$_2$(CO)H (ca. 60%) as a major product over a period of 2 days.

3.7. Synthesis of [Cp*Mo(PMe$_3$)$_3$H$_2$][HCO$_2$]

A solution of Cp*Mo(PMe$_3$)$_3$H (64 mg, 0.14 mmol) in pentane (10 ml) was treated with a solution of HCO$_2$H (6 mg, 0.20 mmol) in pentane (5 ml). The mixture was filtered after stirring for 2 h at r.t., and the residue was washed with pentane (2 × 5 ml) and dried in vacuo to give [Cp*Mo(PMe$_3$)$_3$H$_2$][HCO$_2$] as a pale brown solid (30 mg, 43%). ^{1}H-NMR (C$_6$D$_6$): −4.94 [br. q, $^2J_{P-H} = 49$, 2H, 2MoH], 1.16 [m, 27H, 3P(CH_3)$_3$], 1.46 [s, 15H, C$_5$(CH_3)$_5$], 9.43 [s, 1H, HCO$_2$]. ^{31}P{^{1}H}-NMR (C$_6$D$_6$): 2.6 [s]. ^{31}P{selective ^{1}H−Me}-NMR (C$_6$D$_6$): 2.6 [t, $^2J_{P-H} = 49$]. IR data (KBr disk, cm^{-1}): 1946 [ν(Mo–H)], 1662 [ν(C=O)].

3.8. Conversion of [Cp*Mo(PMe$_3$)$_3$H$_2$][HCO$_2$] to Cp*Mo(PMe$_3$)$_2$(CO)H

A solution of [Cp*Mo(PMe$_3$)$_3$H$_2$][HCO$_2$] (ca. 10 mg) in C$_6$D$_6$ (1 ml) was heated at 80 °C overnight. The reaction was monitored by ^{1}H-NMR spectroscopy which demonstrated the formation of Cp*Mo(PMe$_3$)$_2$-(CO)H (ca. 70%), Me$_3$PO and H$_2$ after 1 day.

3.9. Reactivity of Cp*Mo(PMe$_3$)$_2$(CO)H towards HCO$_2$H

A solution of Cp*Mo(PMe$_3$)$_2$(CO)H (ca. 10 mg) in C$_6$D$_6$ (1 ml) was treated with HCO$_2$H (20 mg) at r.t. The pale yellow solution immediately changed to orange giving initially Cp*Mo(PMe$_3$)$_2$(CO)(η^1-O$_2$CH), which subsequently decomposed to Cp*Mo(PMe$_3$)$_2$-(CO)H when all the HCO$_2$H originally present was converted to CO$_2$ and H$_2$. ^{1}H-NMR for Cp*Mo(PMe$_3$)$_2$(CO)(η^1-O$_2$CH) (C$_6$D$_6$): 1.11 [d, $^2J_{P-H} = 8$, 18H, 2P(CH_3)$_3$], 1.52 [s, 15H, C$_5$(CH_3)$_5$], 8.61 [t, $^4J_{P-H} = 2$, 1H, O$_2$CH]. ^{31}P{^{1}H}-NMR (C$_6$D$_6$): 18.3 [s]. MS: $m/z = 458$ [M$^+$]. The formate complex is only observed in the presence of free HCO$_2$H. Also, if the reaction is carried out at 80 °C, the formic acid is catalytically decomposed to CO$_2$ and H$_2$ within 1 day.

3.10. Reaction of Cp*Mo(PMe$_3$)$_2$(CO)H with MeCO$_2$H

A solution of Cp*Mo(PMe$_3$)$_2$(CO)H (ca. 10 mg) in C$_6$D$_6$ (1 ml) was treated with MeCO$_2$H (10 mg) at 80 °C. ^{1}H-NMR spectroscopy demonstrated that the quantitative formation of Cp*Mo(PMe$_3$)$_2$(CO)(η^1-O$_2$CMe) was complete within 1 day. ^{1}H-NMR (C$_6$D$_6$): 1.25 [d, $^2J_{P-H} = 8$, 18H, 2P(CH_3)$_3$], 1.60 [s, 15H, C$_5$(CH_3)$_5$], 2.07 [s, 3H, O$_2$CCH_3]. ^{31}P{^{1}H}-NMR

(C$_6$D$_6$): 19.5 [s]. ^{13}C-NMR (C$_6$D$_6$): 11.6 [q, $^1J_{C-H} = 127$, 5C, C$_5$(CH_3)$_5$], 18.0 [qm, $^1J_{C-H} = 130$, 6C, 2P(CH_3)$_3$], 26.6 [q, $^1J_{C-H} = 126$, 1C, O$_2$CCH_3], 103.7 [s, 5C, C_5(CH$_3$)$_5$], 176.1 [t, $^3J_{P-C} = 2$, 1C, O$_2$$CCH_3$], CO [not located]. IR data (in pentane): 1802 [ν(C≡O)], 1623 [ν(C=O)]. MS: $m/z = 472$ [M$^+$].

3.11. Reaction of Cp*Mo(PMe$_3$)$_2$(CO)H with EtCO$_2$H

A solution of Cp*Mo(PMe$_3$)$_2$(CO)H (ca. 10 mg) in C$_6$D$_6$ (1 ml) was treated with EtCO$_2$H (10 mg) at 120 °C. ^{1}H-NMR spectroscopy demonstrated that the formation of Cp*Mo(PMe$_3$)$_2$(CO)(η^1-O$_2$CEt) as a major product (ca. 80%) was complete within 1 day. ^{1}H-NMR (C$_6$D$_6$): 1.22 [t, $^3J_{H-H} = 7$, 3H, O$_2$CCH$_2$CH_3], 1.28 [d, $^2J_{P-H} = 9$, 18H, 2P(CH_3)$_3$], 1.65 [s, 15H, C$_5$(CH_3)$_5$], 2.27 [q, $^3J_{H-H} = 7$, 2H, O$_2$CCH_2CH$_3$]. ^{13}C-NMR (C$_6$D$_6$): 11.7 [q, $^1J_{C-H} = 127$, 5C, C$_5$(CH_3)$_5$], 11.7 [q, $^1J_{C-H} = 126$, 1C, O$_2$CCH$_2$$CH_3$], 17.9 [qm, $^1J_{C-H} = 132$, 6C, 2P(CH_3)$_3$], 33.1 [q, $^1J_{C-H} = 125$, 1C, O$_2$CCH$_2$CH$_3$], 103.7 [s, 5C, C_5(CH$_3$)$_5$], 180.0 [s, 1C, O$_2$$CCH_2CH_3$], CO [not located]. ^{31}P{^{1}H}-NMR (C$_6$D$_6$): 19.3 [s]. IR data (in pentane): 1802 [ν(C≡O)], 1622 [ν(C=O)].

3.12. X-ray structure determination of Cp*Mo(PMe$_3$)$_2$(CO)(η^1-O$_2$CMe)

X-ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector and crystal data, data collection and refinement parameters are summarized in Table 1. The structure was solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 5.03) [23]. Hydrogen atoms on carbon were included in calculated positions.

4. Summary

In conclusion, Cp*Mo(PMe$_3$)$_3$H undergoes carbonyl abstraction reactions with a variety of reagents, including CO$_2$, (CH$_2$O)$_n$, MeOH and HCO$_2$H to yield Cp*Mo(PMe$_3$)$_2$(CO)H, which is a catalyst for the decarboxylation of HCO$_2$H to CO$_2$ and H$_2$.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 166448 for compound Cp*Mo(PMe$_3$)$_2$(CO)(η^1-O$_2$CMe). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2

Table 1
Crystal, intensity collection and refinement data for $Cp*Mo(PMe_3)_2(CO)(\eta^1-O_2CMe)$

	$Cp*Mo(PMe_3)_2(CO)(\eta^1-O_2CMe)$
Lattice	Orthorhombic
Empirical formula	$C_{19}H_{36}O_3P_2Mo$
Formula weight	470.36
Space group	*Pbca*
a (Å)	14.709(1)
b (Å)	10.048(1)
c (Å)	31.672(2)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	4680.9(6)
Z	8
Temperature (K)	238
Radiation (λ, Å)	0.71073
D_{calc} (g cm^{-3})	1.335
μ (Mo–K$_\alpha$) (mm^{-1})	0.711
θ maximum (°)	28.3
Number of data	5468
Number of parameters	239
R_1	0.0715
wR_2	0.1556
Goodness-of-fit	1.071

1EZ, UK (Fax: + 44-1223-336033; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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