

Carbonyl abstraction reactions of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}$ with CO_2 , $(\text{CH}_2\text{O})_n$, HCO_2H , and MeOH : the synthesis of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ and the catalytic decarboxylation of formic acid

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Abstract

$\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}$ undergoes carbonyl abstraction reactions with a variety of reagents, including CO_2 , $(\text{CH}_2\text{O})_n$, HCO_2H , and MeOH to yield $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$. The reaction between $\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}$ and HCO_2H has been studied by ^1H -NMR spectroscopy, which indicates that the initial interaction involves protonation of the molybdenum center to give $[\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}_2][\text{HCO}_2]$; upon heating to 80°C , however, $[\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}_2][\text{HCO}_2]$ is converted to the carbonyl complex $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$. In the presence of excess HCO_2H , $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ reacts further to yield $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})(\eta^1\text{-O}_2\text{CH})$; the latter complex undergoes decarboxylation at 80°C and regenerates $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$. Thus, $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ serves as a catalyst for the decomposition of HCO_2H to CO_2 and H_2 . Although the formate complex $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})(\eta^1\text{-O}_2\text{CH})$ has not been isolated, the molecular structure of the acetate derivative $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})(\eta^1\text{-O}_2\text{CMe})$ has been determined by X-ray diffraction. © 2002 Published by Elsevier Science B.V.

Keywords: Synthesis; Carbonyl abstraction; Catalytic decarboxylation

1. Introduction

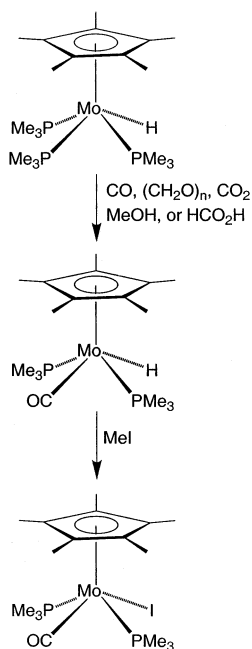
We have previously reported the pentamethylcyclopentadienyl molybdenum trimethylphosphine complexes $\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}$, $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2\text{H}_3$, and $\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}$, together with their use to prepare dinuclear complexes that contain sulfur bridges, e.g. $[\text{Cp}^*\text{Mo}(\mu\text{-SMe})_2]$ and $[\text{Cp}^*\text{Mo}(\mu\text{-S})(\mu\text{-SH})_2]$ [1]. In this paper, we describe further studies on $\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}$ that highlight its ability to abstract CO from a variety of substrates to form $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$, a catalyst for decarboxylation of formic acid.

2. Results and discussion

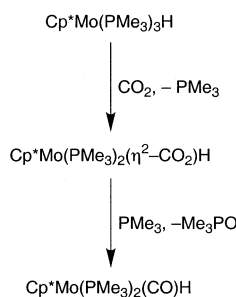
$\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}$ reacts readily with CO at 80°C to yield the carbonyl complex $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ (Scheme 1). The clean synthesis of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ is notable in the sense that $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ has been previously described in the literature, but was not obtained in pure form. Specifically, $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ was generated as a mixture with $\text{Cp}^*\text{Mo}(\text{PMe}_3)(\text{CO})_2\text{H}$ upon reaction of: (i) $[\text{Cp}^*\text{Mo}(\text{CO})_3(\text{PMe}_3)]^+$ with LiAlH_4 ; and (ii) $[\text{Cp}^*\text{Mo}(\text{CO})_4]^+$ with LiAlH_4 in the presence of PMe_3 [2]. It is also important to note that the data reported previously for $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ 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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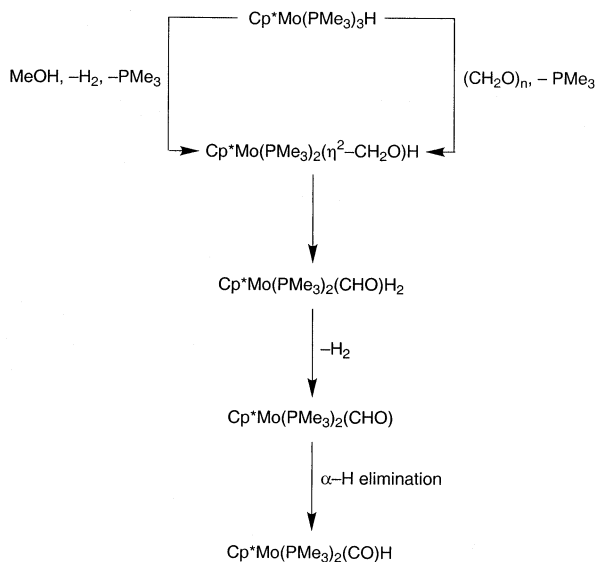
E-mail address: parkin@chem.columbia.edu (G. Parkin).



Scheme 1.



Scheme 2.



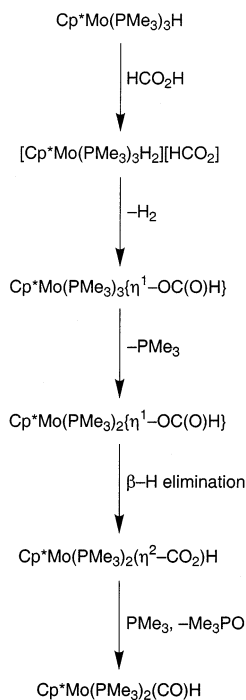
Scheme 3.

$(\text{PMe}_3)_2(\text{CO})\text{H}$ as synthesized by reaction of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}$ with CO is provided by the formation of the iodide derivative $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{I}$ upon reaction with MeI (Scheme 1).

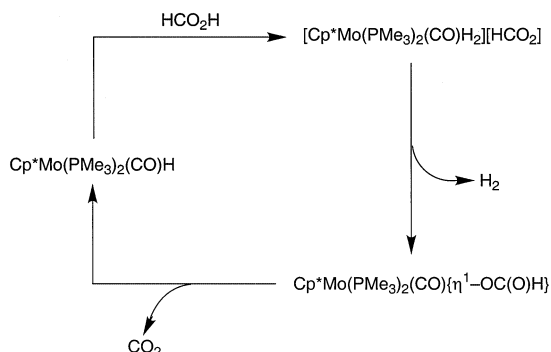
Of more interest than forming $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ by displacement of PMe_3 with CO , $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ is also obtained upon reaction of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}$ with a variety of other reagents, including, CO_2 , paraformaldehyde, MeOH , and HCO_2H (Scheme 1). For the reaction between $\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}$ and CO_2 , $^1\text{H-NMR}$ spectroscopy demonstrates that the formation of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ 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 predated. For example, the reaction of $\text{Re}(\text{PMe}_3)_5\text{H}$ with CO_2 yields the carbonyl complex $\text{Re}(\text{PMe}_3)_4(\text{CO})(\eta^1\text{-O}_2\text{CH})$, 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*- $\text{Cr}(\text{PMe}_3)_4(\text{CO})_2$, $\text{Mo}(\text{PMe}_3)_5(\text{CO})$, $\text{W}(\text{PMe}_3)_5(\text{CO})$, and *trans*- $\text{Fe}(\text{PMe}_3)_4(\text{CO})_2$ [4]. Furthermore, $\eta^2\text{-CO}_2$ complexes are known to decompose to carbonyl derivatives. For example, $\text{Ni}(\text{PCy}_3)_2(\text{CO}_2)$ decomposes to $\text{Ni}(\text{PCy}_3)_2(\text{CO})_2$, while $\text{Fe}(\text{PMe}_3)_4(\text{CO}_2)$ decomposes to $\text{Fe}(\text{PMe}_3)_3(\text{CO})(\text{CO}_3)$ [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 $\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}$ and CO_2 involves initial displacement of PMe_3 and generation of a CO_2 adduct, $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\eta^2\text{-CO}_2)\text{H}$, which undergoes an oxygen atom abstraction with the liberated PMe_3 to yield the carbonyl complex $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ (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 $\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}$ with MeOH to generate, inter alia, $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ 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) $\alpha\text{-H}$ 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



Scheme 4.



Scheme 5.

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

The reaction between $\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}$ and HCO_2H has been studied by ^1H -NMR spectroscopy, which indicates that the initial interaction involves protonation of the molybdenum center to give $[\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}_2][\text{HCO}_2]$ (Scheme 4). The presence of two hydride ligands in $[\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}_2]^+$ is confirmed by the observation of a triplet ($J_{\text{P-H}} = 49\text{ Hz}$) in the $^{31}\text{P}\{^1\text{H-Me}\}$ selectively decoupled NMR spectrum.

Precedent for the formation of $[\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}_2]^+$ is provided by the observation that the analogous complexes $[\text{CpMo}(\text{PMe}_3)_3\text{H}_2][\text{BF}_4]$ [15] and $[\text{CpW}(\text{PMe}_3)_3\text{H}_2][\text{BF}_4]$ [16] have been obtained by reactions of $\text{CpM}(\text{PMe}_3)_3\text{H}$ ($\text{M} = \text{Mo}, \text{W}$) with HBF_4 . Upon heating to 80°C , however, $[\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}_2][\text{HCO}_2]$ is converted to the carbonyl complex $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$, accompanied by elimination of H_2 and Me_3PO . The reaction is proposed to occur via reductive elimination of H_2 , followed by coordination of formate, to yield $\text{Cp}^*\text{Mo}(\text{PMe}_3)_3(\eta^1\text{-O}_2\text{CH})$. Subsequent dissociation of PMe_3 and β -hydrogen elimination would generate the CO_2 complex $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\eta^2\text{-CO}_2)\text{H}$ (Scheme 4). As suggested above, oxygen abstraction from the coordinated CO_2 by PMe_3 would generate $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ and Me_3PO .

Although $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ is obtained by reaction of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}$ with one equivalent of HCO_2H , $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ reacts further with HCO_2H to generate an orange species that has been characterized by ^1H -NMR spectroscopy and mass spectrometry as $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})(\eta^1\text{-O}_2\text{CH})$. However, upon heating to 80°C , $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})(\eta^1\text{-O}_2\text{CH})$ undergoes decarboxylation and regenerates $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ [17]. Thus, $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ serves as a catalyst for the decomposition of HCO_2H 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 $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ mediated decarboxylation of formic acid is illustrated in Scheme 5. In this regard, it is worth noting that the iodide analogue $\text{Cp}^*\text{Mo-}$

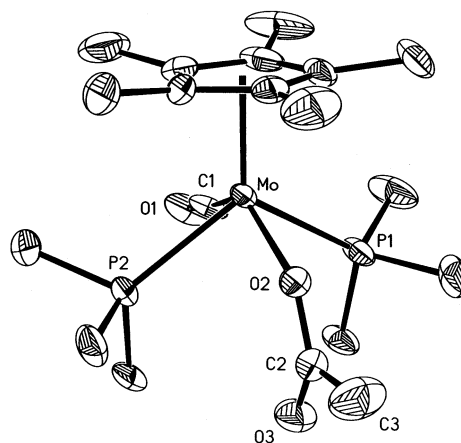


Fig. 1. Molecular Structure of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})(\eta^1\text{-O}_2\text{CMe})$. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): Mo–C(1) 1.874(9), Mo–O(2) 2.167(4), Mo–P(1) 2.462(2), Mo–P(2) 2.454(2), C(1)–O(1) 1.200(9), C(2)–O(2) 1.277(8), C(2)–O(3) 1.212(8), 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).

(PMe₃)₂(CO)I is ineffective as a catalyst for the decomposition of HCO₂H, thereby clearly indicating the important role that the hydride ligand plays in the catalytic cycle. Support for the formation of Cp*Mo(PMe₃)₂(CO)(η¹-O₂CH) is provided by the observation that Cp*Mo(PMe₃)₂(CO)H reacts with MeCO₂H and EtCO₂H to give Cp*Mo(PMe₃)₂-(CO)(η¹-O₂CMe) and Cp*Mo(PMe₃)₂(CO)(η¹-O₂CEt), respectively, and Cp*Mo(PMe₃)₂(CO)(η¹-O₂CMe) has been structurally characterized by X-ray diffraction (Fig. 1). In contrast to Cp*Mo(PMe₃)₂(CO)(η¹-O₂CH), however, Cp*Mo(PMe₃)₂(CO)(η¹-O₂CMe) and Cp*Mo(PMe₃)₂(CO)(η¹-O₂CEt) are stable towards elimination of CO₂ 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 (CH₄) techniques. Elemental analyses were measured using a Perkin–Elmer 2400 CHN Elemental Analyzer. ¹H-NMR spectra were recorded on Varian VXR-200 (200.057 MHz), VXR-300 (299.943 MHz), and VXR-400 (399.95 MHz) spectrometers. ¹³C- and ³¹P-NMR spectra were recorded on a Varian VXR-300 spectrometer. ¹H and ¹³C chemical shifts are reported in ppm relative to SiMe₄ (δ = 0) and were referenced internally with respect to the protio solvent impurity (δ = 7.15 for C₆D₅H and δ = 7.26 for CHCl₃) and the ¹³C resonances (δ = 128.0 for C₆D₆ and δ = 77.0 for CDCl₃), respectively. ³¹P-NMR chemical shifts are reported in ppm relative to 85% H₃PO₄ (δ = 0) and were referenced using P(OMe)₃ (δ = 141.0) as external standard. All coupling constants are reported in Hz. Cp*Mo-(PMe₃)₃H was obtained by the literature method [1].

3.2. Synthesis of Cp*Mo(PMe₃)₂(CO)H

A solution of Cp*Mo(PMe₃)₃H (100 mg, 0.22 mmol) in C₆H₆ (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(PMe₃)₂(CO)H as a brown solid (85 mg, 95%). Anal. Calc. for

C₁₇H₃₄MoOP₂: 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). ¹H-NMR (C₆D₆): -6.85 [t, ²J_{P–H} = 78, 1H, MoH], 1.31 [d, ²J_{P–H} = 8, 18H, 2P(CH₃)₃], 1.91 [s, 15H, C₅(CH₃)₅]. ¹³C-NMR (C₆D₆): 12.5 [q, ¹J_{C–H} = 126, 5C, C₅(CH₃)₅], 25.0 [dq, ¹J_{C–H} = 127, ¹J_{C–P} = 28, 6C, 2 P(CH₃)₃], 100.6 [s, 5C, C₅(CH₃)₅], 253.3 [dt, ²J_{C–P} = 29, ²J_{C–H} = 3, 1C, CO]. ³¹P{¹H}-NMR (C₆D₆): 29.8 [s].

3.3. Synthesis of Cp*Mo(PMe₃)₂(CO)I

A solution of Cp*Mo(PMe₃)₂(CO)H (50 mg, 0.12 mmol) in C₆H₆ (10 ml) was treated with excess CH₃I (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(PMe₃)₂(CO)I as an orange solid. Anal. Calc. for C₁₇H₃₃IMoOP₂: 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). ¹H-NMR (C₆D₆): 1.48 [d, ²J_{P–H} = 8, 18H, 2P(CH₃)₃], 1.70 [s, 15H, C₅(CH₃)₅]. ¹³C-NMR (C₆D₆): 12.1 [q, ¹J_{C–H} = 127, 5C, C₅(CH₃)₅], 20.3 [dq, ¹J_{C–H} = 132, ¹J_{C–P} = 24, 6C, 2P(CH₃)₃], 102.1 [s, 5C, C₅(CH₃)₅], 271.0 [t, ²J_{C–P} = 34, 1C, CO]. ³¹P{¹H}-NMR (C₆D₆): 7.2 [s].

3.4. Reaction of Cp*Mo(PMe₃)₃H with CO₂

A solution of Cp*Mo(PMe₃)₃H (ca. 10 mg) in C₆D₆ (1 ml) was heated at 80 °C under CO₂. ¹H-NMR spectroscopy showed the formation of Cp*Mo(CO)-(PMe₃)₂H (ca. 70%) and Me₃PO after 1 day.

3.5. Reaction of Cp*Mo(PMe₃)₃H with (CH₂O)_n

A mixture of Cp*Mo(PMe₃)₃H (ca. 10 mg) and paraformaldehyde (ca. 10 mg) in C₆D₆ (1 ml) was heated at 80 °C. ¹H-NMR spectroscopy showed the formation of Cp*Mo(PMe₃)₂(CO)H (ca. 40%) inter alia. Prolonged heating resulted in subsequent reaction of Cp*Mo(PMe₃)₂(CO)H with paraformaldehyde to form an unidentified complex.

3.6. Reaction of Cp*Mo(PMe₃)₃H with MeOH

A solution of Cp*Mo(PMe₃)₃H (ca. 10 mg) in C₆D₆ (1 ml) was treated with MeOH (ca. 10 mg) heated at

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

3.7. Synthesis of $[\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}_2][\text{HCO}_2]$

A solution of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}$ (64 mg, 0.14 mmol) in pentane (10 ml) was treated with a solution of HCO_2H (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 $[\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}_2][\text{HCO}_2]$ as a pale brown solid (30 mg, 43%). ^1H -NMR (C_6D_6): -4.94 [br. q, $^2J_{\text{P-H}} = 49$, 2H, 2MoH], 1.16 [m, 27H, $3\text{P}(\text{CH}_3)_3$], 1.46 [s, 15H, $\text{C}_5(\text{CH}_3)_5$], 9.43 [s, 1H, HCO_2]. $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): 2.6 [s]. $^{31}\text{P}\{\text{selective } ^1\text{H-Me}\}$ -NMR (C_6D_6): 2.6 [t, $^2J_{\text{P-H}} = 49$]. IR data (KBr disk, cm^{-1}): 1946 [$\nu(\text{Mo-H})$], 1662 [$\nu(\text{C=O})$].

3.8. Conversion of $[\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}_2][\text{HCO}_2]$ to $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$

A solution of $[\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}_2][\text{HCO}_2]$ (ca. 10 mg) in C_6D_6 (1 ml) was heated at 80 °C overnight. The reaction was monitored by ^1H -NMR spectroscopy which demonstrated the formation of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ (ca. 70%), Me_3PO and H_2 after 1 day.

3.9. Reactivity of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ towards HCO_2H

A solution of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ (ca. 10 mg) in C_6D_6 (1 ml) was treated with HCO_2H (20 mg) at r.t. The pale yellow solution immediately changed to orange giving initially $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})(\eta^1\text{-O}_2\text{CH})$, which subsequently decomposed to $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ when all the HCO_2H originally present was converted to CO_2 and H_2 . ^1H -NMR for $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})(\eta^1\text{-O}_2\text{CH})$ (C_6D_6): 1.11 [d, $^2J_{\text{P-H}} = 8$, 18H, $2\text{P}(\text{CH}_3)_3$], 1.52 [s, 15H, $\text{C}_5(\text{CH}_3)_5$], 8.61 [t, $^4J_{\text{P-H}} = 2$, 1H, O_2CH]. $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): 18.3 [s]. MS: $m/z = 458$ [M^+]. The formate complex is only observed in the presence of free HCO_2H . 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 $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ with MeCO_2H

A solution of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ (ca. 10 mg) in C_6D_6 (1 ml) was treated with MeCO_2H (10 mg) at 80 °C. ^1H -NMR spectroscopy demonstrated that the quantitative formation of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})(\eta^1\text{-O}_2\text{CMe})$ was complete within 1 day. ^1H -NMR (C_6D_6): 1.25 [d, $^2J_{\text{P-H}} = 8$, 18H, $2\text{P}(\text{CH}_3)_3$], 1.60 [s, 15H, $\text{C}_5(\text{CH}_3)_5$], 2.07 [s, 3H, O_2CCH_3]. $^{31}\text{P}\{^1\text{H}\}$ -NMR

(C_6D_6): 19.5 [s]. ^{13}C -NMR (C_6D_6): 11.6 [q, $^1J_{\text{C-H}} = 127$, 5C, $\text{C}_5(\text{CH}_3)_5$], 18.0 [qm, $^1J_{\text{C-H}} = 130$, 6C, $2\text{P}(\text{CH}_3)_3$], 26.6 [q, $^1J_{\text{C-H}} = 126$, 1C, O_2CCH_3], 103.7 [s, 5C, $\text{C}_5(\text{CH}_3)_5$], 176.1 [t, $^3J_{\text{P-C}} = 2$, 1C, O_2CCH_3], CO [not located]. IR data (in pentane): 1802 [$\nu(\text{C}\equiv\text{O})$], 1623 [$\nu(\text{C=O})$]. MS: $m/z = 472$ [M^+].

3.11. Reaction of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ with EtCO_2H

A solution of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$ (ca. 10 mg) in C_6D_6 (1 ml) was treated with EtCO_2H (10 mg) at 120 °C. ^1H -NMR spectroscopy demonstrated that the formation of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})(\eta^1\text{-O}_2\text{CET})$ as a major product (ca. 80%) was complete within 1 day. ^1H -NMR (C_6D_6): 1.22 [t, $^3J_{\text{H-H}} = 7$, 3H, $\text{O}_2\text{CCH}_2\text{CH}_3$], 1.28 [d, $^2J_{\text{P-H}} = 9$, 18H, $2\text{P}(\text{CH}_3)_3$], 1.65 [s, 15H, $\text{C}_5(\text{CH}_3)_5$], 2.27 [q, $^3J_{\text{H-H}} = 7$, 2H, $\text{O}_2\text{CCH}_2\text{CH}_3$]. ^{13}C -NMR (C_6D_6): 11.7 [q, $^1J_{\text{C-H}} = 127$, 5C, $\text{C}_5(\text{CH}_3)_5$], 11.7 [q, $^1J_{\text{C-H}} = 126$, 1C, $\text{O}_2\text{CCH}_2\text{CH}_3$], 17.9 [qm, $^1J_{\text{C-H}} = 132$, 6C, $2\text{P}(\text{CH}_3)_3$], 33.1 [q, $^1J_{\text{C-H}} = 125$, 1C, $\text{O}_2\text{CCH}_2\text{CH}_3$], 103.7 [s, 5C, $\text{C}_5(\text{CH}_3)_5$], 180.0 [s, 1C, $\text{O}_2\text{CCH}_2\text{CH}_3$], CO [not located]. $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): 19.3 [s]. IR data (in pentane): 1802 [$\nu(\text{C}\equiv\text{O})$], 1622 [$\nu(\text{C=O})$].

3.12. X-ray structure determination of $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})(\eta^1\text{-O}_2\text{CMe})$

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, $\text{Cp}^*\text{Mo}(\text{PMe}_3)_3\text{H}$ undergoes carbonyl abstraction reactions with a variety of reagents, including CO_2 , $(\text{CH}_2\text{O})_n$, MeOH and HCO_2H to yield $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})\text{H}$, which is a catalyst for the decarboxylation of HCO_2H 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 $\text{Cp}^*\text{Mo}(\text{PMe}_3)_2(\text{CO})(\eta^1\text{-O}_2\text{CMe})$. 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(PMe₃)₂(CO)(η¹-O₂CMe)

Cp*Mo(PMe ₃) ₂ (CO)(η ¹ -O ₂ CMe)	
Lattice	Orthorhombic
Empirical formula	C ₁₉ H ₃₆ O ₃ P ₂ Mo
Formula weight	470.36
Space group	<i>Pbca</i>
<i>a</i> (Å)	14.709(1)
<i>b</i> (Å)	10.048(1)
<i>c</i> (Å)	31.672(2)
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ³)	4680.9(6)
<i>Z</i>	8
Temperature (K)	238
Radiation (λ, Å)	0.71073
<i>D</i> _{calc} (g cm ⁻³)	1.335
μ (Mo–Kα) (mm ⁻¹)	0.711
θ maximum (°)	28.3
Number of data	5468
Number of parameters	239
<i>R</i> ₁	0.0715
<i>wR</i> 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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