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SYNTHESIS AND MOLECULAR STRUCTURE OF THE μ-ACETYL COMPLEX $Cp(CO)_2Mo(\mu\text{-}O{=}CCH_3)(\mu\text{-}PPh_2)FeCp(CO)$

TOM S. TARGOS, GREGORY L. GEOFFROY*
Department of Chemistry, The Pennsylvania State University, University Park, PA 16802 (U.S.A.)

and ARNOLD L. RHEINGOLD
Department of Chemistry, The University of Delaware, Newark, DE 19716 (U.S.A.)

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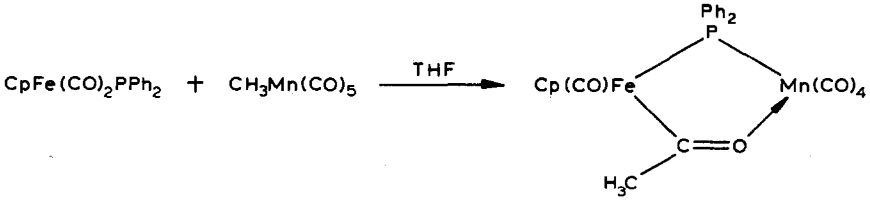
Summary

Reaction of $Cp(CO)_2FePPh_2$ with $CH_3MoCp(CO)_3$ gives the new μ-acetyl and μ-hydride complexes $Cp(CO)_2Mo(\mu\text{-}O{=}CCH_3)(\mu\text{-}PPh_2)FeCp(CO)$ (**2**) and $Cp(CO)Fe(\mu\text{-}H)(\mu\text{-}PPh_2)MoCp(CO)_2$ (**3**) in modest yields. Both complexes have been spectroscopically characterized with **3** further defined by an X-ray diffraction study: $P2_1/c$, a 8.552(2), b 31.052(9), c 9.681(4) Å, β 104.02(3)^0, V 2500(1) Å^3, $Z = 4$, $R = 0.034$, $R_w = 0.038$ for 3800 reflections with $F_0 > 3\sigma(F_0)$. Complex **2** possesses a bridging acetyl ligand with carbon bound to Fe and oxygen bound to Mo. Both spectroscopic and structural data imply considerable oxycarbenoid character in this ligand. The μ-hydride ligand in complex **3** is not acidic and cannot be removed by KOH/EtOH or $Na[N\{SiMe_3\}_2]$.

The FeMn(μ-acetyl) complex **1** was earlier shown to derive from reaction of the metallaphosphine $CpFe(CO)_2PPh_2$ with $CH_3Mn(CO)_5$, eq. 1 [1]. An interesting



(1)

(1)

aspect of this reaction is the unexpected switching of the acetyl coordination mode in forming complex **1**. Since the above reaction is simply the combination of $CH_3Mn(CO)_5$ with the organometallic phosphine $Cp(CO)_2FePPh_2$, an acetyl complex with the acetyl carbon bound to Mn was anticipated, eq. 2 [2].

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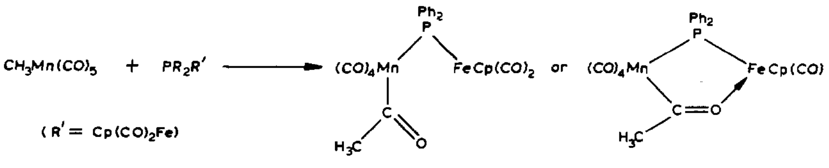
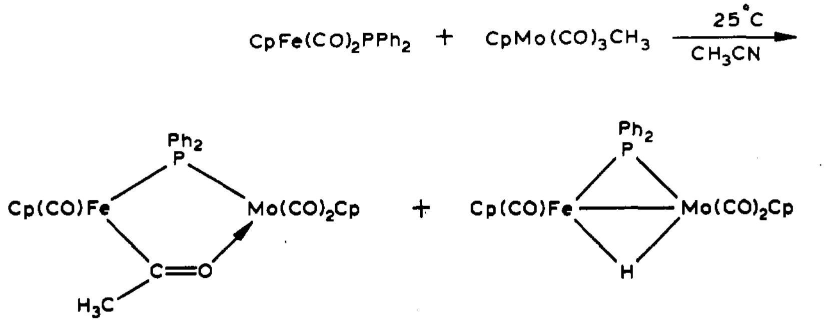


(2)

The objectives of the research described herein were to determine if this synthetic route to μ-acetyl complexes can be generalized to other metal combinations and, if so, to determine whether or not similar μ-acetyl rearrangement occurs. Herein are described the reactions of $Cp(CO)_2FePPh_2$ with $CpMo(CO)_3CH_3$, $CH_3Co(CO)_4$, and $CpFe(CO)_2CH_3$.

Results and discussion

Reaction of $Cp(CO)_2FePPh_2$ *with* $CpMo(CO)_3CH_3$. Of the three methyl complexes mentioned above, only $CpMo(CO)_3CH_3$ leads to a μ-acetyl complex. The organometallic phosphine $CpFe(CO)_2PPh_2$ slowly reacts with $CpMo(CO)_3CH_3$ at 22°C to yield a mixture of the μ-acetyl complex **2** and the μ-hydride complex **3**, eq 3.



(3)

(2) (30%) (3) (7%)

Spectroscopic data imply these two products to be the only compounds formed in the reaction, but extensive decomposition occurs upon chromatographic work-up to give the observed low yields. A key element in this synthesis is the use of CH_3CN as solvent. As has been found for the preparation of other $Cp(CO)_2(PR_3)MoC(O)CH_3$ derivatives [3], use of THF and ether solvents gave greatly reduced yields of **2** and a more complex product mixture.

The new complexes **2** and **3** have been characterized spectroscopically, and complex **2** was further defined by a single-crystal X-ray diffraction study, Fig. 1, which shows the presence of the bridging acetyl ligand with carbon bound to Fe. Thus, as in the synthesis of **1**, rearrangement of the μ-acetyl ligand occurred to give product **2** with the acetyl oxygen attached to the more oxophilic molybdenum atom.

Spectroscopic data for the μ-acetyl complex **2** are consistent with its determined structure, Fig. 1. The ^{13}C NMR spectrum shows the acetyl carbon resonance as a doublet at δ 324.4 ppm (J(C–P) 7.4 Hz) in the region where resonances for other bridging acetyl ligands have been found [1,4,5]. Although the downfield ^{31}P NMR resonance for the μ-PPh_2 ligand of **2** at δ 92.1 ppm would appear to imply the presence of a metal–metal bond [6,7], the crystal structure clearly shows its absence

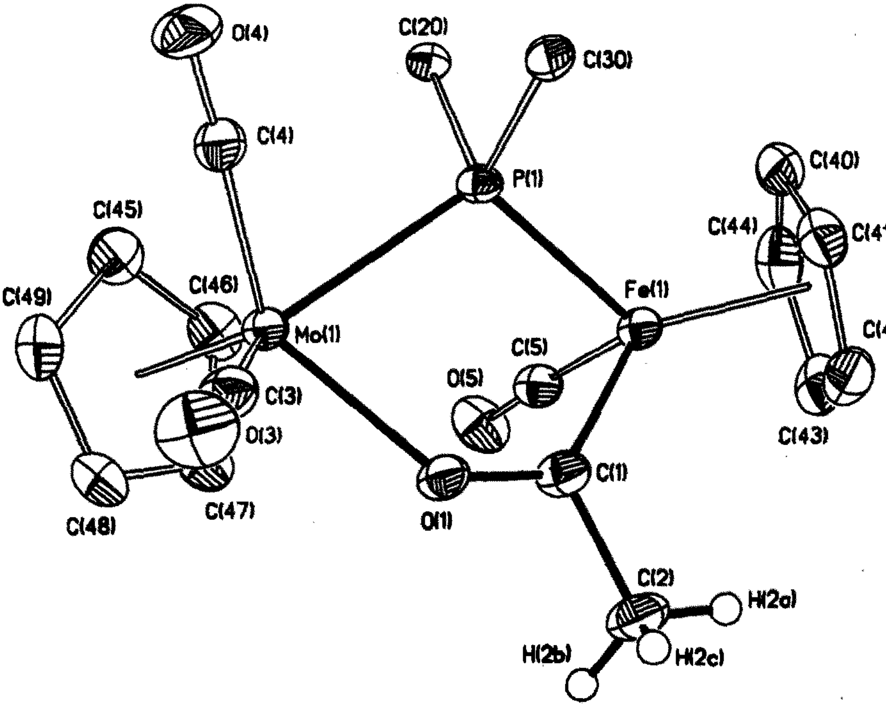


Fig. 1. An ORTEP drawing of $Cp(CO)_2Mo(\mu\text{-}O{=}CCH_3)(\mu\text{-}PPh_2)Fe(CO)Cp$. Thermal ellipsoids are shown at 25% probability. All hydrogen atoms, except H(2a), H(2b) and H(2c) have been removed for clarity.

with an Fe–Mo separation of 3.891(1) Å. However, the structurally similar Fe–Mn complex **1** also shows a downfield μ-PPh_2 resonance at δ 106 ppm [1], and both of these chemical shifts may be attributed to the ring effect noted by Garrou [7a].

The mass spectrum of complex **3** shows a parent ion at m/z 544 consistent with its indicated formulation. Its ^1H NMR spectrum shows two singlets at δ 4.64 and 4.22 ppm for the non-equivalent Cp ligands and a hydride resonance at δ -14.8 ppm (d; J(H–P) 37.6 Hz). The μ-PPh_2 ligand shows a downfield ^{31}P NMR resonance at δ 186.4 ppm, implying the presence of a metal–metal bond [6,7] as required by the 18-electron rule. Although the crystal structure of **3** has not been determined, its spectroscopic data are sufficiently similar to those reported for other $M_2(\mu\text{-}H)(\mu\text{-}PR_2)$ complexes, Table 1, that there can be little doubt of its formulation.

The complexes $(CO)_4\overline{Mn(\mu\text{-}H)\{\mu\text{-}P(C_6H_4\text{-}p\text{-}CH_3)_2\}Mo}(CO)_2Cp$ [8] and $Cp(CO)_2\overline{Mo(\mu\text{-}H)(\mu\text{-}PMe_2)Mo}Cp(CO)_2$ [6,9] have been reported to undergo deprotonation when treated with KOH/EtOH. In contrast, complex **3** did not react under these conditions nor even when the stronger base $Na[N(SiMe_3)_2]$ was used. Thus the hydride ligand in **3** is not acidic. In an attempt to remove the hydrogen as H^-, complex **3** was treated with $[Ph_3C]BF_4$. This gave a slow reaction over 9 h and a complex mixture of products which were not identified due to their instability.

Although the reaction of $CpFe(CO)_2PPh_2$ with $CpMo(CO)_3CH_3$ and $CH_3Mn(CO)_5$ did yield stable bimetallic μ-acetyl products, the reaction of this organome-

TABLE 1

SPECTROSCOPIC DATA FOR BIMETALLIC μ-PPh$_2$, μ-H COMPLEXES

Complex	^{1}H NMR [b]		^{31}P{^{1}H} [b]	M–M	Ref.
	δ (ppm)	J(H–P) (Hz)	δ (ppm)	dist. (Å)	
Cp(CO)Fe(μ-H)(μ-PPh$_2$)$_2$Mo(CO)$_2$Cp (**3**) [a]	−14.8	37.6	186.4	–	this work
Cp(CO)Fe(μ-H)(μ-PPh$_2$)$_2$Mn(CO)$_4$ (**2**) [a]	−18.1d	34.9	176.7	2.806(1)	1
Cp(CO)$_2$Mo(μ-H)(μ-P(C$_6$H$_4$-*p*-CH$_3$)$_2$Mn(CO)$_4$ [a]	−13.91d	31.4	158.1	–	8
Cp(CO)$_2$Mo(μ-H)(μ-PMe$_2$)Mo(CO)$_2$Cp [a]	−11.7d	37	146.4	3.262(7)	6,9
(Bu^{t}NC)(CO)$_4$Mn(μ-H)(μ-PPh$_2$)Mn(CO)$_4$ [c]	−16.18d	35.5	–	2.937(5)	10
(CO)$_3$Mn(μ-H)(μ-PPh$_2$)Mn(CO)$_3$(CNBu^t) [d]	−16.36d	36.5	–	2.959(1)	10b

[a] 22°C, C$_6$D$_6$. [b] (^{1}H NMR) 25°C, acetone-d_6; (^{31}P NMR) −70°C, acetone-d_6. [c] 25°C, C$_6$D$_6$. [d] 25°C, CD$_2$Cl$_2$.

tallic phosphine with CH$_3$Co(CO)$_4$ and CpFe(CO)$_2$CH$_3$ did not give isolable binuclear acyl complexes. The CH$_3$Co(CO)$_4$ reagent decomposes before reaction has a chance to occur and CpFe(CO)$_2$CH$_3$ did not react at temperatures below that at

TABLE 2

CRYSTAL AND INTENSITY DATA FOR Cp(CO)$_2$Mo(μ-O=CCH$_3$)(μ-PPh$_2$)Fe(CO)Cp (**2**)

Mol. Formula	C$_{27}$H$_{23}$FeMoO$_4$P
Mol. Wt. g/mol	594.25
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	8.552(2)
b, Å	31.052(9)
c, Å	9.681(4)
β, deg	104.02(3)
$\bar{V}$, Å^3	2500(1)
ρ(calcd) g cm^{-3}	1.58
Z	4
Crystal dimensions, mm	0.39×0.35×0.20
Temp., °C	21
Radiation	Mo K_α
Scan speed, deg min^{-1}	Variable 4.00–20.0
Scan type	$\omega/2\theta$
Scan range	$\pm 0.9^0$
Stds monitored	3/197 (No decay)
2θ limits, deg	$4.0 \leqslant 2\theta \leqslant 50.0$
Reflections collected	$\pm h, +k, +l$
Number reflections collected	4862
Unique reflections	4403
Unique reflections used $(F_o) > 3\sigma(F_o)$	3800
Weighting Factor, g [a]	0.00013
R [b]	0.034
R_w [c]	0.038
GOF	1.585

[a] Weight $= 1/[\sigma^2(F) + |g|(F^2)]$. [b] $R = \Sigma[|F_0| - |F_c|]/\Sigma|F_0|$. [c] $R_w = [\Sigma w^{1/2}(|F_0| - |F_c|)\Sigma w^{1/2}(F_0)]$.

which $CpFe(CO)_2PPh_2$ decomposes to inert $[CpFe(CO)(\mu\text{-}PPh_2)]_2$. This synthetic approach will obviously be highly sensitive to the stability of the necessary reagents.

Origin of the hydride ligand in complex 3. Several experiments were conducted in an attempt to determine the origin of the hydride ligand in complex **3**. When $CpFe(CO)_2PPh_2$ and $CpMo(CO)_3CH_3$ were allowed to react in CD_3CN solution for 4 days, no deuterated products were observed in the ^2H NMR spectrum of the product mixture, ruling out solvent as the source for the bridging hydride ligand. To probe whether the methyl ligand in $CpMo(CO)_3CH_3$ was the hydride source, the reaction between $CpFe(CO)_2PPh_2$ and $CpMo(CO)_2CD_3$ was explored. This gave a mixture of the deuterated products **2**-d_3, **3**-d_1, and undeuterated complex **3** with the relative amounts of **3** and **3**-d_1 equal to 3/1. This result implies that at least some, but not all, of the μ-hydride ligand is derived from the Mo-CH_3 group, with the rest

TABLE 3

ATOMIC POSITIONAL PARAMETERS FOR $Cp(CO)_2Mo(\mu\text{-}O{=}CCH_3)(\mu\text{-}PPh_2)Fe(CO)Cp$ (**2**)

Atom	x	y	z	U [a]
Mo(1)	4684(1)	5608(1)	2081(1)	34(1)
Fe(1)	6736(1)	6585(1)	741(1)	35(1)
P(1)	6119(1)	6318(1)	2698(1)	33(1)
O(1)	6073(3)	5688(1)	494(2)	45(1)
O(3)	6671(4)	4760(1)	2679(3)	74(1)
O(4)	5849(4)	5507(1)	5350(3)	75(1)
O(5)	3431(3)	6645(1)	−900(3)	66(1)
C(1)	6678(4)	6011(1)	48(4)	44(1)
C(2)	7288(6)	5903(1)	−1257(4)	75(2)
C(3)	5958(5)	5073(1)	2415(4)	49(1)
C(4)	5432(5)	5554(1)	4143(4)	49(1)
C(5)	4739(5)	6615(1)	−211(4)	45(1)
C(20)	4848(4)	6684(1)	3463(3)	37(1)
C(21)	4084(4)	7034(1)	2727(4)	42(1)
C(22)	3055(5)	7289(1)	3272(4)	52(1)
C(23)	2793(5)	7198(1)	4585(4)	54(2)
C(24)	3564(5)	6855(1)	5356(4)	58(2)
C(25)	45176(5)	6596(1)	4807(4)	50(1)
C(30)	7937(4)	6274(1)	4185(3)	40(1)
C(31)	8433(5)	6595(1)	5196(4)	55(2)
C(32)	9822(5)	6542(2)	6282(4)	70(2)
C(33)	10722(5)	6172(2)	6354(4)	77(2)
C(34)	10267(5)	5866(2)	5358(5)	71(2)
C(35)	8902(4)	5912(1)	4266(4)	51(1)
C(40)	8029(5)	7111(1)	1861(5)	59(2)
C(41)	9127(5)	6790(2)	1656(4)	54(1)
C(42)	8930(5)	6740(1)	197(4)	58(2)
C(43)	7725(5)	7014(1)	−503(4)	60(2)
C(44)	7166(5)	7249(1)	536(5)	63(2)
C(45)	2184(5)	5750(1)	2415(5)	59(2)
C(46)	2257(4)	5985(1)	1186(4)	58(2)
C(47)	2375(5)	5687(1)	135(4)	56(2)
C(48)	2398(5)	5272(1)	689(4)	57(2)
C(49)	2262(5)	5306(1)	2102(5)	61(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 4

SELECTED BOND LENGTHS AND BOND ANGLES WITH ESTIMATED STANDARD DEVIATIONS FOR 2

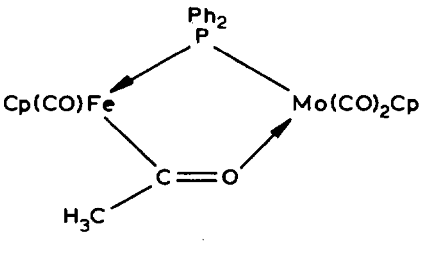
Bond lengths (Å)			
Mo(1)–P(1)	2.528(1)	C(1)–O(1)	1.253(4)
Mo(1)–O(1)	2.177(3)	C(1)–C(2)	1.520(6)
Mo(1)–C(3)	1.970(4)	P(1)–C(20)	1.851(4)
Mo(1)–C(4)	1.950(4)	P(1)–C(30)	1.897(3)
Mo(1)...Fe(1) [a]	3.891(1)	C(3)–O(3)	1.145(5)
Fe(1)–P(1)	2.249(1)	C(4)–O(4)	1.146(4)
Fe(1)–C(1)	1.906(3)	C(5)–O(5)	1.157(4)
Fe(1)–C(5)	1.734(4)		
Bond angles (degrees)			
P(1)–Mo(1)–O(1)	75.5(1)	P(1)–Fe(1)–C(5)	93.7(1)
P(1)–Mo(1)–C(3)	118.8(1)	P(1)–Fe(1)–C(5)	85.8(2)
P(1)–Mo(1)–C(4)	79.3(1)	Mo(1)–P(1)–Fe(1)	108.9(1)
O(1)–Mo(1)–C(3)	80.6(1)	Mo(1)–O(1)–C(1)	132.7(2)
O(1)–Mo(1)–C(4)	129.4(1)	Fe(1)–C(1)–O(1)	127.4(3)
C(3)–Mo(1)–C(4)	74.3(2)	Fe(1)–C(1)–C(2)	121.1(3)
P(1)–Fe(1)–C(1)	87.7(1)	O(1)–C(1)–C(2)	111.4(3)

[a] Non-bonding distance.

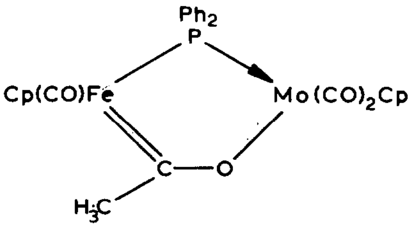
apparently coming from the μ-PPh_2 and cyclopentadienyl ligands or impurities which may be present.

X-ray diffraction study of $Cp(CO)_2Mo(\mu\text{-}O{=}CCH_3)(\mu\text{-}PPh_2)Fe(CO)Cp$ (2). An ORTEP drawing of the inner core of complex **2** is shown in Fig. 1 and crystallographic details, atomic positional parameters, and selected bond lengths and angles are respectively set out in Tables 2–4. The Fe and Mo atoms are bridged by μ-PPh_2 and μ-acetyl ligands with the carbon atom of the latter bound to Fe and the oxygen bound to Mo. The Fe is further coordinated by a Cp ligand and a single CO, while the Mo atom coordinates two CO's and a Cp ligand. The Fe–Mo distance of 3.891(1) Å is consistent with the absence of a metal–metal bond in **2**, as required by the 18-electron rule. The coordination geometry about Fe is the characteristic distorted tetrahedral ligand arrangement found in other CpFe(CO)LX derivatives while the Mo possesses a tetragonal pyramidal ligand arrangement ("4-legged piano-stool") typically found in $CpMo(CO)_2LX$ complexes. The μ-acetyl ligand conveniently fits into the preferred coordination geometries of both metals.

The structural analysis implies that the μ-acetyl ligand in **2** is best described as a hybrid of the acetyl (**2a**) and oxycarbene (**2b**) resonance forms as was also indicated



(2a)



(2b)

for the related FeMn(μ-acetyl) complex **1** [1]. A key structural feature here is the Fe–C(1) distance of 1.906(3) Å which is shorter than the corresponding distances of 1.923(6) and 1.919(8) Å in the two independent molecules of complex **1**. This implies that replacing the $Mn(CO)_4$ fragment by the presumably more oxophilic $Cp(CO)_2Mo$ fragment shifts the structure more towards the oxycarbene form with an $Fe-C_{acetyl}$ double bond. Also consistent with substantial oxycarbenoid character of the μ-acetyl ligand in **2** is the downfield ^{13}C NMR chemical shift of the acetyl carbon at δ 324.4 ppm. This resonance is outside of the usual acetyl range (δ 280–200 ppm) but is within the typical carbene chemical shift range (δ 350–250 ppm) [11].

Experimental

All manipulations were carried out under an atmosphere of dry N_2 utilizing standard Schlenk techniques [12]. All solvents (reagent grade) were dried by appropriate methods and degassed prior to use. $CpFe(CO)_2PPh_2$ [13] $CpMo(CO)_3CH_3$ [14] (**1**), [1], and $CpFe(CO)_2CH_3$ [14] were prepared by literature procedures. The reagents CH_3I and $Na[N(SiMe_3)_2]$ were purchased from Aldrich Chemical Corp. and used as received. Instruments used in this research have been previously described [15]. Elemental analyses were obtained by Schwartzkopf Microanalytical Laboratory, Woodside, NY.

Preparation of $Cp(OC)_2Mo(\mu\text{-}O{=}CCH_3)(\mu\text{-}PPh_2)FeCp(CO)$ (2) and $Cp(CO)\overline{Fe(\mu\text{-}H)(\mu\text{-}PPh_2)Mo}(CO)_2Cp$ (3). A 15 ml CH_3CN solution of $CpMo(CO)_3CH_3$ (0.40 g, 1.35 mmol) was added dropwise to a 15 ml CH_3CN solution of $CpFe(CO)_2PPh_2$ (0.50 g, 1.38 mmol) at 22°C. The dark red solution was stirred for 96 h after which time the solvent was removed by evaporation. The reaction mixture was dissolved in a minimal amount of CH_2Cl_2 and chromatographed on alumina (EM Reagent, activity II-III). Elution with neat hexane gave a small yellow band spectroscopically characterized as $CpMo(CO)_3CH_3$ (~ 0.02 g). Elution with 8% CH_2Cl_2/92% hexane gave first an orange-red band of an unidentified compound (ν(CO) 2024(m), 1942(sh), 1925(s) cm^{-1}, $^{31}P\{^1H\}$ δ 172.5s ppm) which decomposed soon after it was removed from the chromatography column. This was followed by a large red band of $Cp(CO)\overline{Fe(\mu\text{-}H)(\mu\text{-}PPh_2)Mo}(CO)_2Cp$ (**3**). Evaporation of solvent gave **3** as a dark red solid in 7% yield (0.048 g, 0.09 mmol). Further elution with 16% CH_2Cl_2/84% hexane gave an orange-red band of $Cp(CO)_2Mo(\mu\text{-}O{=}CCH_3)(\mu\text{-}PPh_2)Fe(CO)Cp$ (**2**), isolated in 30% yield (0.24 g, 0.40 mmol) following evaporation of solvent. Recrystallization of **2** and **3** from toluene at 0°C yielded analytically pure compounds.

2: Anal. Found: C, 54.50; H, 3.97. $C_{27}H_{23}FeMoO_4P$ calcd.: C, 54.57; H, 3.87%. IR, ν(CO)(THF) 1946(s), 1922(s), 1865(m) cm^{-1}. $^{31}P\{^1H\}$ NMR (22°C, C_6D_6): δ 92.1 (s) ppm. ^1H NMR (22°C, C_6D_6): δ 8.18–6.91 (Ph), 4.83 (s, 5H, Cp), 3.98 (s, 5H, Cp), 2.44 (s, CH_3) ppm. $^{13}C\{^1H\}$ NMR (22°C, THF/C_6D_6): δ 324.4 (d, $O{=}CCH_3$, J(C–P) 7.4 Hz), 174.7 (s, br, CO), 96.9 (s, Cp), 45.5 (s, CH_3) ppm. MS(FD): $m/z = 596$ (M^+).

3: Found: C, 54.27; H, 4.15. $C_{25}H_{21}FeMoO_3P$ calcd.: C, 54.37; H, 3.81%. IR, ν(CO)(THF) 1972(sh), 1925(s), 1862(m) cm^{-1}. $^{31}P\{^1H\}$ (22°C, C_6D_6): δ 186.4s ppm. ^1H (22°C, C_6D_6): δ 7.97–6.86 (Ph), 4.64 (s, 5H, Cp), 4.22 (s, 5H, Cp), −14.8 ppm (d, 1H, μ-H, J(HP) 37.6 Hz). MS(EI), m/z 554 (M^+), 526 ($M^+ -$ CO), 498 ($M^+ -$ 2CO), 470 ($M^+ -$ 3CO).

Attempted deprotonation of 3 with KOH/EtOH and $Na[N(SiMe_3)_2]$. In separate experiments, complex **3** (0.056 g, 0.10 mmol) was combined with excess KOH in ethanol by the method described in ref. 8 and with $Na[N(SiMe_3)_2]$ in THF. The reactions were performed at 22°C and monitored by IR and ^{31}P NMR spectroscopy, but no reaction occurred in either case.

Reaction of $CH_3Co(CO)_4$ with $CpFe(CO)_2PPh_2$. Methyl iodide (0.024 ml, 0.386 mmol) was added via syringe to a THF solution of $Na[Co(CO)_4]$ (0.075 g, 0.386 mmol) at −41°C. The reaction was stirred for 0.5 h and the clear solution became yellow-brown as $CH_3Co(CO)_4$ formed. At this point, a 10 ml THF solution of $CpFe(CO)_2PPh_2$ (0.14 g, 0.386 mmol) was added, and the solution was stirred for 0.5 h at −41°C and then slowly warmed to 22°C. The IR spectrum showed ν(CO) bands at 2063(m), 2030(m), 1961(w), 1885(s,br) cm^{-1}, but the $^{31}P\{^1H\}$ NMR spectrum (22°C, THF/benzene-d_6) showed numerous peaks indicating a complex mixture of products which did not separate well upon chromatography.

Reaction of $CpFe(CO)_2CH_3$ with $CpFe(CO)_2PPh_2$. A 15 ml CH_3CN solution of $CpFe(CO)_2CH_3$ (0.15 g, 0.782 mmol) was added dropwise to a 15 ml CH_3CN solution of $CpFe(CO)_2PPh_2$ (0.28 g, 0.782 mmol) at 22°C. The dark red solution was allowed to stir for 24 h, but IR monitoring showed no reaction. The solution was then refluxed for 24 h and then cooled to 22°C but again with no reaction of $CpFe(CO)_2CH_3$. However, all of the $CpFe(CO)_2PPh_2$ reagent had decomposed.

X-Ray diffraction study of $Cp(CO)_2Mo(\mu\text{-}O{=}CCH_3)(\mu\text{-}PPh_2)FeCp(CO)$ (2). Orange-red crystals of complex **2** were grown by slow evaporation of a saturated hexane solution. The crystals were attached to a glass fiber with epoxy cement and data were collected on a Nicolet R3 diffractometer using graphite-monochromated Mo-K_α radiation. Data collection and refinement procedures used were as previously reported [16]. Pertinent crystal and intensity data are given in Table 2. An empirical absorption correction was applied using ψ-scan data from close-to axial reflections (abs. coeff. 11.8 cm^{-1}; trans. coeff., max–min 0.403–0.367). A profile fitting procedure was applied to the data to improve the precision of the measurement of weak reflections. No correction for decay was required.

The structure was solved and refined using the Nicolet SHELXTL (version 4.0) programs. The direct methods technique (SOLV) yielded the positions of the molybdenum and iron atoms. All other non-hydrogen atoms were determined by difference Fourier techniques. All non-hydrogen atoms were refined anisotropically using blocked-cascade, least-squares refinement methods. The hydrogen atoms were placed in idealized positions with d(C–H) = 0.96 Å, and assigned thermal parameters equal to 1.2 times the isotropic equivalent value for the atoms to which they are attached. The final difference map showed a highest peak of 0.40 $eÅ^{-3}$ at a distance of 1.45 Å from Mo(1) and 1.15 Å from P(1). Table 3 lists atomic positional parameters for the non-hydrogen atoms and selected bond lengths and angles are given in Table 4. Tables of thermal parameters, complete bond distances and angles, calculated hydrogen atom parameters, and structure factors are available from the author upon request.

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References

1 R.P. Rosen, J.B. Hoke, R.R. Whittle, G.L. Geoffroy, J.P. Hutchinson, and J.A. Zubieta, Organometallics, 3 (1984) 846.

2 For interesting examples of μ-acetyl head-to-tail switching see C.M. Jensen, Y.J. Chen and H.D. Kaesz, J. Am. Chem. Soc., 106 (1984) 4046.

3 P.J. Craig, and M.H. Green, J. Chem. Soc. A, (1968) 1978.

4 (a) B. Longato, J.R. Norton, J.C. Huffman, J.A. Marsella, and K.G. Caulton, J. Am. Chem. Soc., 103 (1981) 209; (b) J.A. Marsella, J.C. Huffman, K.G. Caulton, B. Longato, and J.R. Norton, ibid., 104 (1982) 6360.

5 C.M. Jensen, C.B. Knobler, and H.D. Kaesz, J. Am. Chem. Soc., 106 (1984) 5926.

6 J.L. Petersen, and R.P. Stewart, Inorg. Chem., 19 (1980) 186.

7 (a) P.E. Garrou, Chem. Rev., 81 (1981) 229; (b) A.J. Carty, S.A. MacLaughlin and N.J. Taylor, J. Organomet. Chem., 204 (1981) C27; (c) A.J. Carty, Adv. Chem. Ser., 196 (1982) 163.

8 C.P. Casey, and R.M. Bullock, Organometallics, 3 (1984) 1100.

9 (a) R.G Hayter, Inorg. Chem., 2 (1963) 1031; (b) R.J. Doedens, and L.F. Dahl, J. Am. Chem. Soc., 87 (1965) 2576.

10 (a) R.J. Doedens, W.T. Robinson, and J.A. Ibers, J. Am. Chem. Soc., 89 (1967) 4323; (b) J.A. Iggo, M.J. Mays, P.R. Raithby, and K. Hendrick, J. Chem. Soc., Dalton Trans., (1983) 205.

11 B.E. Mann, and B.F. Taylor, ^{13}C NMR Data for Organometallic Compounds, Academic Press, London, 1981.

12 D.F. Shriver, The Manipulation of Air Sensitive Compounds, McGraw Hill, New York, 1969.

13 J.C.T.R. Burckett-St. Laurent, R.J. Haines, C.R. Nolte, and N.D.C.T. Steen, Inorg. Chem., 19 (1980) 577.

14 T.S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3 (1956) 104.

15 M.J. Breen, P.M. Shulman, G.L. Geoffroy, A.L. Rheingold, and W.C. Fultz, Organometallics, 3 (1984) 782.

16 A.L. Rheingold, and P.J. Sullivan, Organometallics, 2 (1983) 327.