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The reactions of *trans*-[$MoH_4(Ph_2PCH_2CH_2PPh_2)_2$] with $RCO_2C{\equiv}CH$ (R = Me or Et) in the presence of acids. Preparation of hydrido-σ-alkenyl complexes of molybdenum(IV)

Neimat Kashef and Raymond L. Richards

School of Chemistry and Molecular Sciences and Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9QJ, Sussex (Great Britain)

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Abstract

Reaction of *trans*-[$MoH_4(dppe)_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) with $RCO_2C{\equiv}CH$ (R = Me or Et) in the presence of HBF_4 in tetrahydrofuran (thf) gives the carboxylato-σ-alkenyl complexes [$MoH_2\{\overline{CH{=}CHC(O)}OR\}(dppe)_2]BF_4$, whereas if HBr is used as acid, decarboxylation of the alkenyl ligand occurs to give the complexes [$MoBrH_2(CH{=}CHR)(dppe)_2$].

The enzyme nitrogenase reduces alkynes to alkenes and evolves dihydrogen. Because of our interest in the reactions of dinitrogen and related complexes as models for the behaviour of the nitrogenase active metal centre, generally assumed to be molybdenum, we thought it appropriate to study the reactions of alkynes with molybdenum-dinitrogen and molybdenum-hydride complexes. The reactions with dinitrogen complexes give alkyne, alkynyl, and, in the presence of acids, alkylidyne and alkylidene complexes [1,2]. Henderson has shown that the relatively inert complex *trans*-[$MoH_4(dppe)_2$] reacts rapidly with a number of substrates, including $PhC{\equiv}CH$, in the presence of acids such as HBF_4. We therefore extended our studies of alkyne reactions to this hydride in the expectation of obtaining alkyne complexes of the type reported by Henderson, e.g. [$MoF(HC{\equiv}CPh)(dppe)_2]BF_4$ [3]. We found instead, however, that σ-alkenyl complexes were produced in our system. Some of the results have been mentioned in a preliminary communication [2] and we now present full details of the preparation and characterization of these compounds.

Results and discussion

A yellow suspension of [$MoH_4(dppe)_2$] with an excess of $RCO_2C{\equiv}CH$ (R = Me or Et) in thf changed to a pink solution on addition of an excess of acid. Pink solids

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Table 1

Hydride-alkenyl complexes of molybdenum

Complex	Colour	Analysis (%) [a]		IR (cm^{-1}) [b]	NMR ($C^2H_2Cl_2$) [c]			
		C	H			δ(ppm)	Assignment	
[MoH$_2${HC=CHC(O)OCH$_3$}(dppe)$_2$]BF$_4$	Pink	65.3 (64.9)	5.2 (5.3)	1565m (C=O) 1451m (C=C)	^{1}H	9.2s,br	Mo-C*H*=C*H*	(2H)
						8–6mu	Ph	(40H)
						3.4s	C*H*$_3$	(3H)
						2.5–2.1br	P-C*H*$_2$	(8H)
						−6.8mu	Mo-*H*	(2H)
					^{31}P	−100s [d]		
					^{19}F	−156s	BF$_4^-$	
					^{13}C	174s	*C*O	
						157s [e]	Mo-*C*H=CH	
						132.7–120.3mu	Ph	
						118s [e]	Mo-CH=*C*H	
						31s [f]	P-*C*H$_2$	
						28s [g]	O-*C*H$_3$	
[MoH$_2${HC=CHC(O)OEt}(dppe)$_2$]BF$_4$	Pink	64.8 (65.2)	5.3 (5.4)	1565m (C=C) 1450m (C=C)	^{1}H	9.8br	Mo-C*H*=C*H*	(2H)
						8–6 mu	Ph	(40H)
						4.1qua [h]	C*H*$_2$-CH$_3$	(2H)
						2.5–2.1br	P-C*H*$_3$	(8H)
						0.9t [h]	CH$_2$-C*H*$_3$	(3H)
						−4.25mu	Mo-*H*	(2H)
					^{31}P	−100s [d]		
					^{19}F	−156s	BF$_4^-$	
					^{31}C	174s	*C*O	
						157.3s [e]	Mo-*C*H=CH	
						132–120mu	Ph	
						118s [e]	Mo-CH=*C*H	
						67.55s [i]	*C*H$_2$-CH$_3$	
						28s [j]	CH$_2$-*C*H$_3$	
						25s [f]	P-*C*H$_2$	

$[MoH_2Br(HC{=}CHMe)(dppe)_2]$	Pink	64.5	4.8	1460m (C=C)	^1H	9.8br	Mo-C*H*-C*H*	(2H)
		(64.9)	(5.1)			8–6mu	Ph	(40H)
						3.6s	$C\mathit{H}_3$	(3H)
						2.1–1.9mu	$P\text{-}C\mathit{H}_2$	(8H)
						−4.5qui [k]	Mo-*H*	(2H)
					^{31}P	−55s		
					^{13}C	145.7s [l]	Mo*C*H=CH	
						138.9–126.8mu	Ph	
						115.45 [m]	MoCH=*C*H	
						30.14s [n]	$P\text{-}\mathit{C}H_2$	
						14.29s [o]	$\mathit{C}H_3$	
$[MoH_2Br(HC{=}CHEt)(dppe)_2]$	Red	65.0	5.1	1465m (C=C)	^1H	9.8br	Mo-C*H*=C*H*	(2H)
		(65.2)	(5.2)			8–6mu	Ph	(40H)
						4.5 [p]	$CH_2\text{-}C\mathit{H}_3$	(3H)
						2.1–1.89br	$P\text{-}C\mathit{H}_2$	(8H)
						1.2qua [p]	$C\mathit{H}_2\text{-}CH_3$	(2H)
						−4.4qui [k]	Mo-*H*	(2H)
					^{31}P	−55.65s		
					^{13}C	146s [l]	Mo-*C*H=CH	
						138.8–126mu	Ph	
						115s [m]	Mo-CH=*C*H	
						50.85s [q]	CH_2CH_3	
						29.4s	$P\text{-}\mathit{C}H_2$	
						25.4s [r]	$\mathit{C}H_2\text{-}CH_3$	

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[a] Calculated values in parentheses. [b] KBr disc. [c] ^1H and ^{13}C rel $SiMe_3$, $\delta(P)$ rel. $P(OMe)_3$ as standards. [d] At room temperature. A complex multiplet is observed at lower temperatures (−80 °C). [e] Becomes a doublet $J(CH) = 163$ Hz in the ^1H undecoupled spectrum. [f] Becomes a triplet $J(CH) = 121$ Hz in the ^1H undecoupled spectrum. [g] Becomes a quartet $J(CH) = 140$ Hz in the ^1H undecoupled spectrum. [h] $J(HH) = 6.83$ Hz. [i] Becomes a triplet $J(CH) = 146.5$ Hz in the ^1H undecoupled spectrum. [j] Becomes a quartet $J(CH) = 146.5$ Hz in the ^1H undecoupled spectrum. [k] $J(PH) = 30$ Hz. [l] Becomes a doublet $J(CH) = 160$ Hz in the ^1H undecoupled spectrum. [m] Becomes a doublet $J(CH) = 158$ Hz in the ^1H undecoupled spectrum. [n] Becomes a triplet $J(CH) = 125$ Hz in the ^1H undecoupled spectrum. [o] Becomes a quartet $J(CH) = 121$ Hz in the ^1H undecoupled spectrum. [p] $J(HH) = 6.83$ Hz. [q] Becomes a quartet $J(CH) = 148.5$ Hz in the ^1H undecoupled spectrum. [r] Becomes a triplet $J(CH) = 148.5$ Hz in the ^1H undecoupled spectrum. m = medium, mu = multiplet, br = broad, s = singlet, t = triplet, qui = quintet, qua = quartet.

separated, and these analysed as $[MoH_2\{CH{=}CHC(O)OR\}(dppe)_2]BF_4$ (**A**) when $HBF_4 \cdot OEt_2$ was used and as $[MoBrH_2(CH{=}CHR)(dppe)_2]$ (**B**) when HBr gas was used. The reactions thus proceed as in eqs. 1 and 2.

$$[MoH_4(dppe)_2] + HC{\equiv}CCO_2R \xrightarrow[HBF_4]{thf}$$

$$\underset{(\mathbf{A})}{[MoH_2\{CH{=}CHC(O)OR\}(dppe)_2]BF_4} + H_2 \quad (1)$$

$$[MoH_4(dppe)_2] + HC{\equiv}CCO_2R \xrightarrow[HBr]{thf}$$

$$\underset{(\mathbf{B})}{[MoBrH_2(CH{=}CHR)(dppe)_2]} + CO_2 + H_2 \quad (2)$$

The compounds were formulated as hydrido-σ-alkenyl complexes on the basis of their analytical and spectroscopic properties as shown in Table 1.

Both sets of compounds, **A** and **B**, show (C=C) IR bands at around 1450 cm^{-1} and the bands at around 1565 cm^{-1} in compounds **A** are assigned to (C=O) vibrations. The bathochromic shift of these latter vibrations from ~ 1650 cm^{-1} in the free alkynes implies that the carbonyl group ligates the metal as shown in Fig. 1.

This structure is analogous to that proposed as one isomer of the compounds $[MoH\{CH{=}C(CH_3)C(O)OR\}(dppe)_2]$ (R = Et, Pr^i or Bu^n), which are analogues of **A** and were obtained by the thermal or photochemically induced reactions of $[MoH_4(dppe)_2]$ with various alkyl methacrylates [4].

The hydrido-σ-alkenyl structure for complexes **A** and **B** was deduced mainly from their ^{1}H, ^{13}C and ^{31}P NMR spectra. For example, the ^{1}H NMR spectrum of (**A**, R = Me) in CD_2Cl_2 at room temperature exhibits a Mo-hydride signal at δ −6.8 ppm as a poorly-resolved multiplet (possibly doublet of quintets) due to coupling with the phosphorus nuclei, and a broad signal at 9.2 ppm integrating for two vinylic protons. The other signals due to ligating propiolate and dppe appear in the normal region, as shown in Table 1.

In the ^{13}C NMR spectra of (**A**, R = Me), signals were observed at 28 ppm (CH_3), 118 (β-carbon), 174 ppm (carbonyl carbon *C*O), and at 157 ppm (α-carbon attached to molybdenum). Assignment of each signal was confirmed by proton-coupled spectra, which revealed the expected doublets centred at 118 ppm and 157 ppm [J(CH) = 163 Hz] (Table 1). The spectrum of (**A**, R = Et) was similarly assigned (Table 1).

The ^{13}P{^{1}H} NMR spectrum of complexes **A** in CD_2Cl_2 at room temperature showed a complicated pattern. These complexes, which are rigid at room tempera-

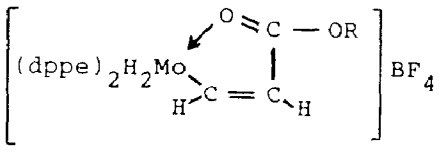


Fig. 1. Chelation of σ-alkenyl ligands.

ture, become stereochemically non-rigid as the temperature is raised, and eventually produce a sharp singlet at 100 ppm, indicating that the four P nuclei have become magnetically equivalent. These observations are quite similar to those reported for the analogous $[\overline{\mathrm{MoH\{CH{=}C(CH_3)C(O}})\mathrm{OR\}(dppe)_2}]$ complexes [4]. On the other hand, the $^{31}P\{^1H\}$ NMR spectra of complexes **B** consisted of a single sharp resonance, at ~ 55 ppm, that seems to be independent of temperature, indicating a *trans*-configuration of the phosphine ligands at all the temperatures used. The ^{19}F spectra of complexes **B** revealed a singlet at −156 ppm assignable to the $[BF_4]$ anion, and conductivity measurements showed that the above complexes are 1 : 1 electrolytes, in agreement with the proposed formulation.

The ^1H NMR spectra of complexes **B** also revealed a hydride signal as a quintet centred at ~ −4.5 ppm [J(PH) 30 Hz] and a broad resonance at 9.8 ppm, both integrating for two protons (Table 1). Their ^{13}C NMR spectra indicated that a decarboxylation had occurred during the reaction with HBr. For example, the spectrum of (**B**, R = Me) contained resonances at 145.7 and at 115.4 ppm, values typical of olefinic carbons, and showed C–H coupling (Table 1), and so could be assigned to α-carbon (carbon attached to Mo) and β-carbon, respectively, but no resonance around 170 ppm assignable to a carbonyl carbon was observed. The remaining resonances due to methyl or ethyl groups, etc. are listed in Table 1. Moreover, no IR band assignable to (C–O) stretching was observed.

Both **A** and **B** are soluble in common organic solvents but are difficult to purify. Thus characterisation was performed with samples which had been specially purified by repeated crystallisation from thf/ether. The complexes are moderately insensitive to air in the solid state, but are quite unstable to air in solution.

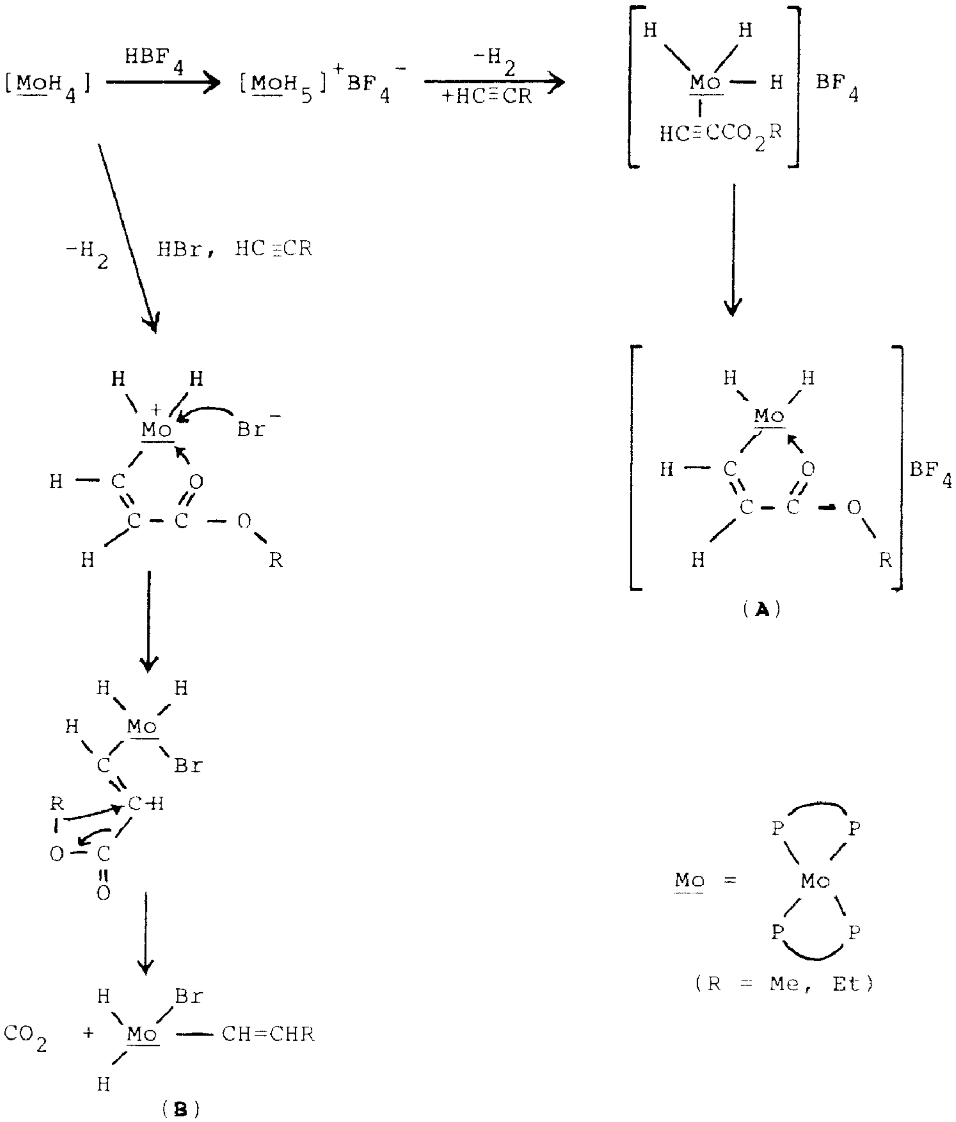
Experiments using $[WH_4(dppe)_2]$ under the same conditions did not produce alkenyl complexes; the only product was $[WH_5(dppe)_2]^+$, which appeared to be inert towards the alkynes.

Mechanism of reactions

The first step in the above reactions seems to be the formation of the penta-hydride cation $[MoH_5(dppe)_2]^+$, which was shown to be formed in Henderson's [3,5] reaction of $[MoH_4(dppe)_2]$ with PhC≡CH in the presence of an excess of HBF_4. Isolation of $[WH_5(dppe)_2]^+$ in this work seems to provide further evidence of the formation of such an intermediate, but it appears that the W-analogue does not undergo H_2 loss and is therefore the final product.

The protonation of the Mo complex causes H_2 loss, so that the acetylene complex $[MoH_3(HC_2{\equiv}CCO_2R)(dppe)_2]^+$ (R = CH_3 or Et) can possibly be formed as an intermediate, as shown in Scheme 1.

In contrast to the product from Henderson's reaction (the acetylene complex, $[MoF(PhC{\equiv}CH)(dppe)_2]BF_4$), the ligating (C≡C) in the present case is hydrogenated to produce the hydrido-σ-alkenyl complexes. The reaction with HBr follows a different route from that with HBF_4, as the former is accompanied by a decarboxylation process. Presumably, this is connected with the ability of Br^-, a stronger nucleophile than BF_4^-, to compete effectively with the C=O in coordination to the metal, preventing C=O binding, so that decarboxylation can occur as shown in Scheme 1. It appears to be coordination of CO to the metal in the BF_4 salts that stabilises the alkenyl ligand towards decarboxylation.



Scheme 1. Proposed mechanism of formation of the σ-alkenyl complexes.

Experimental

Reactions were carried out under dry dinitrogen and in solvents dried by standard methods then freshly distilled under dinitrogen. Vacuum and/or Schlenk techniques were employed for all manipulations. Literature methods were used to prepare the hydride complexes of molybdenum and tungsten [6,7]. Other chemicals were reagent or Analar grade, and used as supplied.

Infrared spectra were recorded on a Perkin–Elmer 577 spectrometer, with KBr discs. NMR spectra were recorded by C. Macdonald of the A.F.R.C. I.P.S.R. Nitrogen Fixation Laboratory, University of Sussex, and by Dr. A. Avent of the University of Sussex, with Bruker WM360, JEOL FX90Q and Bruker WP80 spectrometers. Samples were sealed under dinitrogen. Tetramethylsilane, (TMS) was used as internal standard for ^{1}H NMR and ^{13}C NMR spectra and trimethylphosphite (TMP) as an external standard for ^{31}P NMR spectra. Analyses were carried out by C. Macdonald or by Butterworth Laboratories Ltd. Conductivities, in nitromethane, were measured with a Portland Electronics bridge.

Preparation of $[MoH_2\{CH{=}CHC(O)CH_3\}(dppe)_2]BF_4$

A solution of $[MoH_4(dppe)_2]$ 0.5 g, (5.5×10^{-4} mmol) in tetrahydrofuran (15 ml) was treated at room temperature with an excess of methylpropiolate (0.3 ml) and an ethereal solution of fluoroboric acid (8 molar excess) and the mixture was kept for for 1 h at room temperature. The resulting pink precipitate was filtered off and washed with diethyl ether. The pink solid was obtained in 78% yield after recrystallisation from a mixture of tetrahydrofuran and diethyl ether. Molar conductivity: 92.1 ohm cm^{-3} mol^{-1} (in nitromethane solution). The ethyl analogue was prepared similarly.

Preparation of $[MoH_2(CH{=}CHCH_3)Br(dppe)_2]$

An excess of gaseous HBr (5 mmol) was introduced on a vacuum line to a solution of $[MoH_4(dppe)_2]$ (0.4 g, 5×10^{-4} mmol) and an excess of methyl propiolate (0.25 ml) in tetrahydrofuran (15 ml) held at $-196\,°$C. When the reaction flask was allowed to warm to $20\,°$ C, a pink solid separated immediately. The solid was filtered off, washed with 2 × 15 ml of dry diethyl ether, and dried in vacuum. Recrystallisation from a tetrahydrofuran–diethyl ether mixture afforded a pink solid (yield 90%). The ethyl analogue was prepared similarly.

Preparation of $[WH_5(dppe)_2]BF_4$

A solution of $[WH_4(dppe)_2]$ 0.5 g (5×10^{-4} mmol) in tetrahydrofuran (13 cm^3) was treated at room temperature with an excess of ethylpropiolate (0.4 ml) and an ethereal solution of fluoroboric acid (8 molar excess) and the mixture kept at room temperature for 1 h. The yellow solution was then reduced in volume and dry diethyl ether was added. This produced a yellow precipitate, which was washed with ether and dried in a vacuum (yield 79%). (Found: C, 58.0; H, 4.8; $WC_{52}H_{53}BF_4P_4$ calc: C, 58.2; H, 5.0%). Its spectroscopic properties were identical to those of an authentic sample of $[WH_5(dppe)_2]BF_4$ prepared by the published procedure [8].

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