Diazoalkane Complexes of Molybdenum and Tungsten *via* Hydrazido(2−) Complexes

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The reaction of $[Mo(N_2)_2(depe)_2]$ (depe = $Et_2PCH_2CH_2PEt_2$) with MeBr affords $[MoBr(NNMe_2)(depe)_2]Br$, whereas EtBr yields both $[MoBr(NNEt)(depe)_2]$ and $[MoBr(NNEt_2)(depe)_2]Br$. Condensation of acetaldehyde with $[MBr(NNH_2)(depe)_2]^+$ (M = Mo or W) gives the diazoalkane complexes $[MBr(NNCHMe)(depe)_2]^+$ which can be used to synthesize alkyldiazenido-compounds by reaction with $Li[AlH_4]$.

We have recently described reactions of alkyl halides (principally bromides) with complexes $[M(N_2)_2(diphosphine)_2]$ (M = Mo or W) to yield alkyldiazenido-complexes[1] and dialkylhydrazido(2−)-complexes.[2] We discovered that the diphosphine $Et_2PCH_2CH_2PEt_2$ (depe) confers unusual properties on the bis(dinitrogen) complexes in these reactions. Thus, $[Mo(N_2)_2(depe)_2]$ and MeBr react relatively slowly to yield a dimethylhydrazido(2−)-complex, with no methyldiazenido-complex detected as an intermediate. On the other hand, $[W(N_2)_2(depe)_2]$ proved inert to methyl bromide, even in refluxing benzene under irradiation, and was recovered unchanged.[3] This paper describes these reactions in more detail, and also the application of a route to alkyldiazenido-complexes *via* diazoalkane derivatives, previously demonstrated for complexes of $Ph_2PCH_2CH_2PPh_2$ (dppe).[4]

Results and Discussion

Although the reaction of $[Mo(N_2)_2(depe)_2]$ with MeBr is such that any diazenido-complex formed reacts rapidly with more MeBr to form the dimethylhydrazido(2−)-complex $[MoBr(NNMe_2)(depe)_2]^+$ so that the diazenido-complex cannot be isolated,[2,3] this is not the case with less strongly donating phosphines. We have already shown that, for dppe analogues, MeBr reacts much more rapidly than EtBr in the second alkylation step,[2] and so employing EtBr with $[Mo(N_2)_2(depe)_2]$ we have now been able to isolate both $[MoBr(NNEt)(depe)_2]$ and $[MoBr(NNEt_2)(depe)_2]^+$.

However, we also prepared $[MoBr(NNEt)(depe)_2]$ by an alternative route, outlined below.

$$[Mo(N_2)_2(depe)_2] \xrightarrow{HBr} [MoBr(NNH_2)(depe)_2]^+ \xrightarrow{MeCHO}$$

$$\underset{(\mathbf{A})}{[MoBr(NNCHMe)(depe)_2]^+} \xrightarrow{Li[AlH_4]} [MoBr(NNEt)(depe)_2]$$

The structures of these complexes were confirmed by the usual spectral criteria. Thus complex (**A**) shows a band at 1 578 cm^{-1} assignable to ν(C=N), and the unique NC*H*Me proton gives rise to a quartet in the ^{1}H n.m.r. spectrum at δ 8.37 p.p.m., irradiation of which causes collapse of the doublet at δ 1.63 p.p.m. (NCHC*H*$_3$) to a singlet. The complexes all show the singlet in the ^{31}P n.m.r. spectrum characteristic of four equivalent coplanar phosphorus atoms. The new compounds are detailed in Tables 1 and 2.

We have also produced diazomethane complexes of molybdenum by reaction of $[Mo(N_2)_2(depe)_2]$ with methylene bromide (isolated in small yield and characterized spectroscopically) and of $[MoF(NNH_2)(depe)_2]^+$ with acetaldehyde. This last material will be described elsewhere.

The tungsten complex $[WBr(NNH_2)(depe)_2]^+$ also reacts with acetaldehyde to form a diazoethane complex, characterized fully both spectroscopically and analytically. This should provide a route to alkyldiazenido-complexes of W and depe, *via* nucleophilic attack on the co-ordinated diazoethane. These are, of course, not obtainable by reaction of the dinitrogen complex with alkyl halide.

In summary, the reactions of $[M(N_2)_2(depe)_2]$ and its derivatives seem to differ in degree rather than in kind from those of $[M(N_2)(dppe)_2]$ and its derivatives, the yields being smaller and the products being much more difficult to isolate.

Experimental

The complexes $[M(N_2)_2(depe)_2]$[5] and $[MBr(NNH_2)(depe)_2]Br$ were obtained as described elsewhere.[6] Reagents were obtained commercially, and purified as appropriate.

All reactions and compound manipulations were carried out in Schlenk apparatus under dinitrogen, or on vacuum lines. All solvents were dried and distilled under dinitrogen before use. I.r. spectra were recorded in KBr discs on a Perkin-Elmer 527

Table 1. Analytical data for new complexes

Complex	Colour	M.p. (°C)	Λ_M / Ω^{-1} cm^2 mol^{-1}	Analysis[a] (%) C	H	N	Yield (%)
(**1**) $[MoBr(NNMe_2)(depe)_2]Br$	Pink-brown	242	84.5	37.1 (36.4)	7.40 (7.45)	3.80 (3.85)	23
(**2**) $[MoBr(NNEt_2)(depe)_2]Br$	Maroon	235	68.5	38.1 (38.2)	7.55 (7.70)	3.70 (3.70)	13
(**3**) $[MoBr(NNEt)(depe)_2]$	Red	132		40.0 (40.9)	7.20 (8.20)	4.25 (4.35)	18/30[b]
(**4**) $[MoBr(NNCHMe)(depe)_2]Br$	Green	175	77.2	36.8 (36.5)	7.25 (7.20)	3.95 (3.85)	66
(**5**) $[WBr(NNCHMe)(depe)_2]Br$	Green	110	68.0	32.7 (32.5)	6.60 (6.40)	3.15 (3.45)	61

[a] Calculated values in parentheses. [b] 18% *via* diazoethane complex, 30% *via* $[Mo(N_2)_2(depe)_2]$.

Table 2. Spectral properties of the new complexes

Complex	I.r. ($\mathrm{cm^{-1}}$) (KBr discs)	^{1}H N.m.r. (p.p.m.)[a]	^{31}P N.m.r. (p.p.m.)[b]	^{13}C N.m.r. (p.p.m.)[c]
(1)	1 360 ν(N=N)	0.89—1.35 (m, 24, $\mathrm{CH_3}$), 1.53—2.20 (m, 24, $\mathrm{CH_2}$), 2.90 (s, 6, $\mathrm{NCH_3}$) ($\mathrm{CDCl_3}$)	−95.8	
(2)	1 360 ν(N=N)	0.92—1.08 (t, 6, $\mathrm{NCH_2C}\mathit{H}_3$), 1.15—1.37 (m, 24, $\mathrm{CH_3}$), 1.60—2.35 (m, 24, $\mathrm{CH_2}$), 3.05—3.30 (q, 4, $\mathrm{NCH_2}$) ($\mathrm{CD_2Cl_2}$)	−96.5	
(3)	1 495 ν(N=N)	0.72—0.88 (t, 3, $\mathrm{NCH_2C}\mathit{H}_3$), 1.11—1.25 (m, 24, $\mathrm{CH_3}$), 1.57—2.34 (m, 24, $\mathrm{CH_2}$), 2.94—3.18 (q, 2, $\mathrm{NCH_2}$) ($\mathrm{CDCl_3}$)	−91.3	
(4)	1 578 ν(C=N)	0.8—1.4 (m, 24, $\mathrm{CH_3}$), 1.63 (d, 3, $\mathrm{CHC}\mathit{H}_3$), 1.7—2.3 (m, 24, $\mathrm{CH_2}$), 8.37 (q, 1, CH) ($\mathrm{CDCl_3}$)	−99.37	−171.4 (N*C*HCH$_3$)
(5)	1 570 ν(C=N)	0.6—1.5 (m, 24, $\mathrm{CH_3}$), 1.52 (d, 3, $\mathrm{CHC}\mathit{H}_3$), 1.6—2.6 (m, 24, $\mathrm{CH_2}$), 8.61 (q, 1, CH) ($\mathrm{CDCl_3}$)	−113.17 [*J*(WP) = 264.2 Hz]	−196.7 (N*C*HCH$_3$)

[a] m = Multiplet, s = singlet, d = doublet, t = triplet, and q = quartet. [b] With respect to trimethyl phosphite. [c] With respect to tetramethylsilane.

spectrometer (±2 $\mathrm{cm^{-1}}$). Proton and ^{31}P n.m.r. data were obtained on a JEOL FX-90Q spectrometer using tetramethylsilane and trimethyl phosphite as internal and external standards, respectively, as appropriate. Melting points were obtained under dinitrogen on an Electrothermal melting-point apparatus. Electrical conductivities were obtained in solution in nitromethane using a Portland Electronics conductivity bridge. Analyses were by Mr. C. Macdonald, AFRC Unit of Nitrogen Fixation.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*bromo*[N′,N′-*dimethylhydrazido*(2—)-N]*molybdenum Bromide*.—To a solution of the appropriate dinitrogen complex (0.54 g, 1.0 mmol) in benzene (30 $\mathrm{cm^3}$) held at −196 °C in a vacuum line was added methyl bromide (1.1 mmol). The solution was warmed to 20 °C, and stirred under tungsten-filament light irradiation for 17 h. The pink-brown *solid* produced was filtered off, washed with pentane (2 × 2 $\mathrm{cm^3}$), and dried *in vacuo*. Yield 0.16 g.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*bromo*[N′,N′-*diethylhydrazido*(2—)-N]*molybdenum Bromide*.—To a solution of the dinitrogen complex (0.50 g, 0.90 mmol) in benzene (30 $\mathrm{cm^3}$) was added ethyl bromide (0.20 g, 1.8 mmol) and the mixture stirred under tungsten-filament light irradiation for 19 h. The red solution obtained was reduced to a red oil at 10^{-3} mmHg (0.133 Pa), which was stirred with methanol (10 $\mathrm{cm^3}$) for 0.5 h. The pink solid which separated was filtered off, and the filtrate again reduced to an oil at 10^{-3} mmHg. This was stirred with diethyl ether (10 $\mathrm{cm^3}$), reduced to a solid at 10^{-3} mmHg, and recrystallised from dichloromethane–diethyl ether as large maroon *crystals*. Yield 0.09 g.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*bromo*(*diazoethane*)-*molybdenum Bromide*.—Acetaldehyde (0.74 g, 17 mmol) at −30 °C was distilled under vacuum into a solution of $[\mathrm{MoBr(NNH_2)(depe)_2}]\mathrm{Br}$ (1.17 g, 1.7 mmol) in dichloromethane (50 $\mathrm{cm^3}$) at −196 °C. The mixture was stirred at 20 °C for 20 h and the resultant grey solution taken to dryness at 10^{-3} mmHg. The sticky residue was recrystallised from dichloromethane–diethyl ether as green-grey *crystals*. Yield 0.08 g. The *complex* bis[1,2-bis(diethylphosphino)ethane]bromo(diazoethane)tungsten bromide was prepared similarly from $[\mathrm{WHBr(NNH_2)(depe)_2}]\mathrm{Br_2}$ (0.60 g, 0.69 mmol) and acetaldehyde (*ca.* 10 mmol). Yield 0.45 g.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*bromo*(*diazomethane*)-*molybdenum Bromide*.—To a solution of the molybdenum dinitrogen complex (0.80 g, 1.4 mmol) in benzene (35 $\mathrm{cm^3}$) was added methylene bromide (0.48 g, 2.8 mmol) and the solution stirred under tungsten-filament light irradiation for 72 h. The red solution was reduced to dryness at 10^{-3} mmHg and extracted with hexane (40 $\mathrm{cm^3}$). The residue was treated with thf (39 $\mathrm{cm^3}$), the suspension filtered, and diethyl ether added to the filtrate until it turned slightly turbid. After storing at −5 °C for 7 d, brown *crystals* were filtered off, washed with thf–diethyl ether (1 : 1) (2 × 2 $\mathrm{cm^3}$), and dried *in vacuo*. Yield 0.11 g.

Spectral data and the analogy with the chemistry of the dppe system all confirm the nature of this product, which was not, however, completely characterised since analytical data were not obtained.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*bromo*(*ethyldiazenido*)-*molybdenum*.—(*a*) The molybdenum diazoethane complex (0.47 g, 0.64 mmol) was suspended in diethyl ether (20 $\mathrm{cm^3}$) and a large excess (× 10) of $\mathrm{Li[AlH_4]}$ added. The mixture was stirred at 20 °C for 1 h, and the red-orange solution taken to dryness at 10^{-3} mmHg. The solid was extracted with benzene (20 $\mathrm{cm^3}$) and the extract reduced to a sticky red solid at 10^{-3} mmHg. This was extracted with diethyl ether (25 $\mathrm{cm^3}$), leaving an unidentified yellow solid. The extract, reduced to dryness at 10^{-3} mmHg, gave a red solid, which was extracted with hexane (15 $\mathrm{cm^3}$). The extract was reduced to *ca.* 5 $\mathrm{cm^3}$ at 10^{-3} mmHg, and stored at −5 °C for 12 h. The initial pink-brown solid was rejected, but after another 3 d, large red *crystals* were produced, filtered off, washed with cold pentane (2 × 0.2 $\mathrm{cm^3}$), and dried *in vacuo*. Yield 0.12 g.

(*b*) A mixture of $[\mathrm{Mo(N_2)_2(depe)_2}]$ (0.59 g, 1.1 mmol) and EtBr (0.25 g, 2.3 mmol) in benzene (40 $\mathrm{cm^3}$) was stirred at 20 °C under tungsten-filament irradiation for 19 h. The red solution was reduced to an oil at 10^{-3} mmHg, and the oil stirred in methanol (10 $\mathrm{cm^3}$) for 0.5 h. The pink solid was filtered off and rejected, and the filtrate reduced to an oil at 10^{-3} mmHg. The oil was stirred in diethyl ether, taken to dryness, and the residue recrystallised from dichloromethane–hexane as red *crystals*. Yield 0.20 g.

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