# New Diazenido-complexes of Molybdenum(IV), Tungsten(IV), and Rhenium(III)

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The reaction of $[MCl_4(Ph_2PCH_2CH_2PPh_2)]$ with phenylhydrazine produces the complexes $[MCl_3(N_2Ph)(Ph_2PCH_2CH_2PPh_2)]$ (M = Mo or W). Similar derivatives containing $Et_2PCH_2CH_2PEt_2$ and $PMe_2Ph$ have also been isolated. The structures have been assigned by n.m.r. spectroscopy. An improved synthesis of $[ReCl_2(N_2Ph)(NH_3)(PMe_2Ph)_2]$ is reported. The diazenido-ligand can be quaternised with methyl iodide.

It has been known for some time that diazenido-complexes of transition elements can be synthesised by reaction of an appropriate transition-metal compound with a hydrazine derivative. Examples include the formation of $[Mo(N_2Ph)_2(S_2CNEt_2)_2]$ from $[MoO_2(S_2CNEt_2)_2]$ and phenylhydrazine,[1] and of $[ReCl_2(N_2Ph)(PMe_2Ph)_3]$ and $[ReCl_2(N_2Ph)(NH_3)(PMe_2Ph)_3]$ from $[ReCl_3(PMe_2Ph)_3]$ and phenylhydrazine.[2] The detailed mechanisms, including in particular the fate of the 'excess' of hydrogen atoms, is not known, although it is clear that in the former reaction both $[Mo(N_2Ph)(NHNHPh)(S_2CNEt_2)_2]$ and aerial dioxygen are involved.[1] We here present some additional information regarding such complexes and their mode of formation.

## Results and Discussion

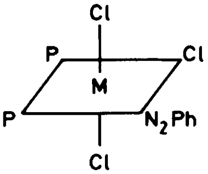
The complexes $[MCl_3(N_2Ph)(dppe)]$ [M = Mo or W, dppe = 1,2-bis(diphenylphosphino)ethane] were obtained from the reaction of $[MCl_4(dppe)]$ with $(Me_3Si)NHNHPh$ (*ca.* 1:1) in benzene at room temperature. The reaction of $[MCl_4(depe)]$ [depe = 1,2-bis(diethylphosphino)ethane, M = Mo or W] is analogous. The reaction of $[MoCl_4(dppe)]$ with a six-fold excess of phenylhydrazine in ethanol yields $[MoCl_2(N_2Ph)_2(dppe)]$ as a purple solid, and the analogous reaction of $[MoCl_3(PMe_2Ph)_3]$ generates $[MoCl_2(N_2Ph)_2(PMe_2Ph)_2]$. Reaction of the latter with $Na(S_2CNEt_2)\cdot 3H_2O$ gives the known compound $[Mo(N_2Ph)_2(S_2CNEt_2)_2]$.[1]

These diazenido-complexes have a band in the i.r. spectra in the range 1 480—1 530 $cm^{-1}$ characteristic of $\nu(N{=}N)$. The $^{31}P$-$\{^1H\}$ n.m.r. spectra of all the diphosphine complexes display a doublet of doublets (AB pattern) consistent with non-equivalent phosphorus nuclei, the only feasible structures being those of (**I**) and (**II**).

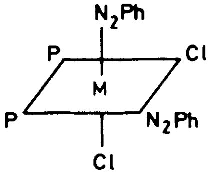
The complex $[MoCl_2(N_2Ph)_2(PMe_2Ph)_2]$ shows a singlet in the $^{31}P$-$\{^1H\}$ n.m.r. spectrum. In the $^1H$ n.m.r. spectrum, the methyl groups give rise to one triplet (due to virtual coupling), and this also indicates a plane of symmetry containing the linear P–Mo–P system.[3] The structure is shown by (**III**). The alternative arrangement with *trans* phosphorus should give rise to two triplets.

None of these complexes possesses an $N_2Ph$ group basic enough to react with HBr in tetrahydrofuran (thf), neither do they react with MeI in benzene, even under reflux. They all would be expected to possess a singly bent NNPh structure, but the nitrogen lone pairs are presumably not easily available, either because they are involved in N–N–Ph $\pi$ bonding or because of the influence of the high-oxidation-state metals.

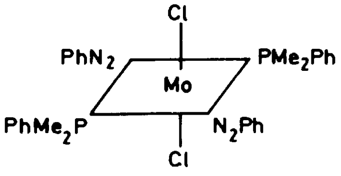
The fate of the excess of hydrogens in these preparative reactions is not clear. It is likely that initial reaction of the metal halogeno-complexes with the hydrazine derivatives forms a reactive hydrazide(1 −) complex. Other workers have shown that $[WCl_4(PMe_2Ph)_2]$ reacts with $(Me_3Si)NHNHPh$ to form $[WCl_3H(N_2HPh)(PMe_2Ph)_2]$[4] which loses the hydride hydrogen during slow crystallisation from $CH_2Cl_2$, but it is not clear how. In addition, $[WCl_4(py)_2]$ (py = pyridine) reacts with $(Me_3Si)NHNHPh$ to form $[WCl_2(N_2Ph)_2(py)_2]$, but the reaction route has not been clarified.[4] In the same reaction, $[WCl_3(NHNHPh)(py)_2]$ may also be formed, but it has not been adequately characterised.



(**I**)



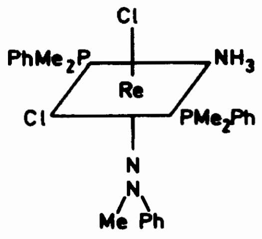
(**II**)



(**III**)

The compound $[ReCl_2(N_2Ph)(NH_3)(PMe_2Ph)_2]$ is obtained in high yield (>70%) by reaction of $[ReCl_4(PMe_2Ph)_2]$ with $PhNHNH_2$ in ethanol. This reaction does not produce any $[ReCl_2(N_2Ph)(PMe_2Ph)_3]$, which always accompanies the formation of the ammine from $[ReCl_3(PMe_2Ph)_3]$.[2] It is tempting to ascribe the formation of the ammine to a series of intramolecular hydrogen shifts between hydrazide(1 −) ligands in an intermediate species containing the grouping $Re(NHNHPh)_2$. The mechanisms of such shifts are unknown, but aniline was isolated from the reaction mixture and identified by both thin-layer chromatography and gas chromatography. Clearly such hydrogen shifts, whether they are inter- or intra-molecular, are common features of the chemistry of hydrazido-complexes.

It has already been reported that $[ReCl_2(N_2Ph)(NH_3)(PMe_2Ph)_2]$ reacts with proton acids to generate $[ReCl_2(N_2HPh)(NH_3)(PMe_2Ph)_2]^+$, whereas $[ReCl_2(N_2Ph)(PMe_2Ph)_3]$ does not react with protons.[2] We have now found that the latter diazenido-complex does not react with MeI, whereas the former reacts with MeI in thf at reflux. The product is $[ReCl_2(N_2MePh)(NH_3)(PMe_2Ph)_2]I$. Its $^{31}P$-$\{^1H\}$ n.m.r. spectrum shows a single phosphorus resonance, and the methyl groups appear in the H n.m.r. spectrum as a pair of triplets. This is consistent with equivalent *trans* phosphorus nuclei, but no plane of symmetry containing the P–Re–P axis.[3] The structure is that shown by (**IV**), similar to that of the



(IV)

phenylhydrazido(2 – )-complex which was determined by *X*-ray structure analysis.[2]

Alkylation of the phenyldiazenido-complex presumably is an $S_N2$ reaction at the carbon of methyl iodide.[5] In the ammine complex, the *exo* nitrogen of the phenyldiazenido-group seems basic (it also reacts with acids), presumably due to the presence of the donor ammonia rather than $PMe_2Ph$. The difference in basicity between the $N_2Ph$ groups in $[ReCl_2(N_2Ph)(PMe_2Ph)_3]$ and $[ReCl_2(N_2Ph)(NH_3)(PMe_2Ph)_2]$ is unlikely to be correlated with the presence of straight or singly bent $N_2Ph$ groups, since the formal electron counts are the same. Consequently, one might expect the NNC(phenyl) angle in both compounds to be between 120 and 150°. The factors affecting basicity and reactivity are probably more subtle than gross geometrical changes.

## Experimental

All reactions were carried out under dry dinitrogen. I.r. spectra were recorded in KBr discs using a Perkin-Elmer 577 spectrometer. N.m.r. spectra were recorded using a JEOL FX-90Q spectrometer, with tetramethylsilane and trimethyl phosphite as external standards for $^1H$ and $^{31}P$ n.m.r. spectra, respectively. Conductivities were obtained using a Portland Electronics conductivity bridge. Melting points were obtained in sealed tubes *in vacuo* and using an Electrochemical melting point apparatus. Analyses were carried out by Mrs. G. Olney (University of Sussex) and Mr. C. Macdonald (A.F.R.C., Unit of Nitrogen Fixation).

The complexes $[MCl_4(dppe)]$ (M = Mo or W),[6] $[ReCl_4(PMe_2Ph_2)]$,[7] $[MoCl_3(PMe_2Ph)_3]$,[8] $[WCl_4(MeCN)_2]$,[9] and $(Me_3Si)NHNHPh$,[10] were obtained by literature methods.

$[1,2$-*Bis(diethylphosphino)ethane*$]$*tetrachloromolybdenum*(IV).—To a suspension of $[MoCl_4(thf)_2]$[8] (2.0 g, 0.53 mmol) in tetrahydrofuran (thf) (120 cm$^3$) was added depe (1.2 g, 5.8 mmol). The suspension changed to brick red, in a green-brown solution. The mixture was reduced to 5 cm$^3$, diethyl ether (30 cm$^3$) added, and the red-brown *solid* filtered off and dried *in vacuo*. Yield: *ca.* 65% (Found: C, 28.0; H, 5.3. $C_{10}H_{24}Cl_4MoP_2$ requires C, 27.0; H, 5.4%).

Since this complex and the related tungsten material (see below) were required only as intermediates, they were not further purified.

$[1,2$-*Bis(diethylphosphino)ethane*$]$*tetrachlorotungsten*(IV)–*Acetonitrile* (1/1).—A mixture of $[WCl_4(MeCN)_2]$ (0.60 g, 1.47 mmol) and depe (0.5 g, 2.4 mmol) in toluene (20 cm$^3$) was heated under reflux for 1.5 h, yielding a brown solution and suspension. The suspension was filtered off and the residue washed with diethyl ether (30 cm$^3$) and dried *in vacuo*. Yield: *ca.* 75% (Found:

**Table.** Analytical and physical data for the complexes

| Complex | Colour | M.p./°C | Yield (%) | Analysis[a] C | H | N | I.r./cm$^{-1}$ (KBr)[b] | Solvent | $^1H(\delta)$[c] | $^{31}P$-{$^1H$}/p.p.m.[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| $[WCl_3(N_2Ph)(dppe)]$ | Brown | 162 | 50 | 48.7<br>(48.4) | 3.1<br>(3.70) | 4.3<br>(3.55) | 1 494s,<br>1 310m | $C_6D_6$ | 8.60—6.50<br>(m, 25 H, Ph)<br>4.50—3.10<br>(m, 4 H, $CH_2$) | –101.48, –101.83<br>(12.7)<br>–129.63, –129.68<br>(12.7) |
| $[MoCl_3(N_2Ph)(dppe)]$ | Red-purple | 169 | 50 | 55.6<br>(54.5) | 4.6<br>(4.75) | 4.4<br>(3.95) | 1 530br,s | $C_6D_6$ | 8.49—6.69<br>(m, 25 H, Ph)<br>4.31—1.50<br>(m, 4 H, $CH_2$) | –102.32, –102.53<br>(7.6)<br>–124.87, –125.08<br>(7.6) |
| $[WCl_3(N_2Ph)(depe)]$ | Brown | 94 | 35 | 33.6<br>(33.7) | 5.2<br>(5.65) | 4.4<br>(4.00) | 1 480s,<br>1 310s | $C_6D_6$ | 8.00—7.30<br>(m, 5 H, Ph)<br>3.0—1.5<br>(br, m, 24 H, $CH_3$ + $CH_2$) | –94.89, –95.38<br>(17.8)<br>–110.44, –110.93<br>(17.8) |
| $[MoCl_3(N_2Ph)(depe)]$ | Red-brown | 79 | 35 | 40.9<br>(41.4) | 6.3<br>(5.65) | 4.8<br>(5.10) | 1 520br,s | $C_6D_6$ | 7.40—6.60<br>(m, 5 H, Ph)<br>2.8—0.4<br>(br, m, 24 H, $CH_3$ + $CH_2$) | –95.73, –96.08<br>(12.7)<br>–115.20, –115.55<br>(13.0) |
| $[MoCl_2(N_2Ph)_2(dppe)]$ | Purple | 185 | 40 | 58.2<br>(58.9) | 4.6<br>(4.40) | 7.6<br>(7.20) | 1 515br,s | $C_6D_6$ | 8.39—6.74<br>(m, 25 H, Ph)<br>3.27—2.13<br>(m, 4 H, $CH_2$) | –95.12, –95.33<br>(7.6)<br>–117.67, –117.88<br>(7.6) |
| $[MoCl_2(N_2Ph)_2(PMe_2Ph)_2]$ | Purple | 185 | 60 | 51.3<br>(51.5) | 5.2<br>(4.95) | 8.9<br>(8.60) | 1 515br,s,<br>1 470s | $C_6D_6$ | 8.12—7.12<br>(m, 15 H, Ph)<br>2.40—2.30<br>(t, 12 H, $CH_3$) | –144.34 |
| $[ReCl_2(N_2MePh)(NH_3)(PMe_2Ph)_2]I$[e] | Pink | 197 | 40 | 34.6<br>(34.6) | 4.2<br>(4.5) | 5.3<br>(5.25) | 1 332m | $CH_2Cl_2$ | 7.30—7.10<br>(m, 15 H, Ph)<br>5.24 (s, br, 3 H, $NH_3$)<br>3.58 (s, br, 3 H, NMe)<br>2.03—1.75<br>(d of t, 12 H, Me) | –171.92 |

[a] Calculated values in parentheses. [b] s = Strong, m = medium, br = broad; region of nitrogen–nitrogen stretching frequency. [c] m = Multiplet, s = singlet, d = doublet, t = triplet, br = broad. [d] All signals singlets, *J* in parentheses in Hz, shifts with respect to external $P(OMe)_3$. [e] $\Lambda_M$ = 83 ohm$^{-1}$ cm$^2$ mol$^{-1}$ in solution in $MeNO_2$.

C, 26.4; H, 4.7; N, 2.7. $C_{12}H_{27}Cl_4NP_2W$ requires C, 25.1; H, 4.7; N, 2.4%).

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*trichloro*(*phenyldiazenido*)*molybdenum*(IV).—To [$MoCl_4$(dppe)] (0,64 g, 1 mmol) in benzene (30 $cm^3$) was added ($Me_3SiNHNHPh$ (0.2 g, 1.1 mmol) and the solution stirred at 20 °C for 20 h. The resultant red-purple solution was reduced *in vacuo* to 2 $cm^3$ and diethyl ether (20 $cm^3$) added to precipitate the *product* as a red-purple solid. The analysis in the Table could not be improved by crystallisation. Indeed, it seems likely that the mono(diazenido)-complex disproportionates in some way in solution to yield the bis(diazenido)-complex. This was not pursued.

Similar procedures were used to prepare [1,2-*bis*(*diphenylphosphino*)*ethane*]*trichloro*(*phenyldiazenido*)*tungsten*(IV). The same method was also used to prepare [1,2-*bis*(*diethylphosphino*)*ethane*]*trichloro*(*phenyldiazenido*)-*molybdenum*(IV) and -*tungsten*(IV).

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*dichlorobis*(*phenyldiazenido*)-*molybdenum*(IV).—To [$MoCl_4$(dppe)] (0.95 g, 1.5 mmol) dissolved in ethanol (30 $cm^3$) was added phenylhydrazine (1.05 $cm^3$, 10.7 mmol) and the mixture heated to 55 °C for 2 h. The red-purple precipitate was filtered off, and recrystallised from benzene–diethyl ether as purple *crystals*.

*Dichlorobis*(*dimethylphenylphosphine*)*bis*(*phenyldiazenido*)-*molybdenum*(IV).—To a solution of [$MoCl_3(PMe_2Ph)_3$] (0.80 g, 1.3 mmol) in ethanol (60 $cm^3$) was added phenylhydrazine (0.83 $cm^3$, 8.4 mmol) and the mixture heated to 75 °C for 0.75 h, during which time it changed from a yellow suspension to a deep red solution. The solvent was removed *in vacuo* yielding an oil. This was dissolved in methanol (30 $cm^3$) and stirred to yield a purple solid which was recrystallised from benzene–pentane as deep purple *crystals*.

*Bis*(NN-*diethyldithiocarbamato*)*bis*(*phenyldiazenido*)*molybdenum*(IV).[1]—To a solution of [$MoCl_2(N_2Ph)_2(PMe_2Ph)_2$] (0.03 g, 0.04 mmol) in methanol (30 $cm^3$) was added $Na(S_2CNEt_2)\cdot 3H_2O$ (0.024 g, 0.11 mmol) and the mixture stirred at 20 °C for 3 d. Reduction in volume yielded black crystals (20%), m.p. 99 °C (lit.,[1] 103 °C) (Found: C, 43.8; H, 5.5; N, 13.3. $C_{22}H_{30}MoN_6S_4$ requires C, 43.8; H, 5.00; N, 13.9%).

*Amminedichlorobis*(*dimethylphenylphosphine*)(*phenyldiazenido*)*rhenium*(III).[2]—To a solution of [$ReCl_4(PMe_2Ph)_2$] (0.23 g, 0.38 mmol) in ethanol (50 $cm^3$) was added phenylhydrazine (0.24 $cm^3$, 2.3 mmol). The mixture was heated to 60 °C for 0.5 h, and the brown solution reduced *in vacuo* to 10 $cm^3$. Addition of hexane (30 $cm^3$) produced a yellow solid, which was filtered off and dried *in vacuo*, yield 70%, m.p. 160—164 °C (decomp.) [lit.,[2] 164—171 °C (decomp.)] (Found: C, 34.6; H, 4.3; N, 5.3. $C_{22}H_{30}Cl_2N_3P_2Re$ requires C, 34.6; H, 4.15; N, 5.25%).

*Amminedichlorobis*(*dimethylphenylphosphine*)[N,N-*methylphenylhydrazido*(2−)-N′]*rhenium*(V) *Iodide*.—A mixture of [$ReCl_2(N_2Ph)(NH_3)(PMe_2Ph)_3$] (0.50 g, 0.63 mmol) and methyl iodide (2 $cm^3$, 32 mmol) in thf (100 $cm^3$) was heated under reflux for 5 h. The volume was reduced to *ca.* 5 $cm^3$ *in vacuo*, and pentane (5 $cm^3$) added, giving a pink-brown *solid*, which was recrystallised from thf–pentane.

## Acknowledgements

We acknowledge financial assistance from the University of Malaysia (to H. M. A.).

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*Received* 30*th October* 1984; *Paper* 4/1852