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SYNTHESIS OF PHENYLDIAZENIDO, PHENYLHYDRAZIDO AND DIORGANOHYDRAZIDO COMPLEXES OF MOLYBDENUM AND TUNGSTEN AND THEIR REACTIONS WITH ACIDS: A COMPARISON WITH ANALOGOUS UNSUBSTITUTED HYDRAZIDO (NNH₂) COMPLEXES. THE CRYSTAL STRUCTURE OF [WCl₂(NN(H)Ph)(PMe₂Ph)₃]

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Abstract—The phenyldiazenido complexes $[MCl(NNPh)(PMe_2Ph)_4]$ (M = Mo, W) and phenyl- and diorganohydrazido(2-) complexes [WCl₂(NN(H)Ph)(PMe₂Ph)₃], [MCl₂ (M = Mo, W; R = R' = Me, R = R' = Ph; M = W, R = Me, $(NNRR')(PMe_2Ph)_3$ R' = Ph, $[MCl_2(NNPh_2)(dppe)(PMe_2Ph)]$ (M = Mo, W; $dppe = Ph_2PCH_2CH_2PPh_2$), $[MCl(NNPh_2)(dppe)_2]Cl (M = Mo, W)$, and $[WCl(NN(Me)Ph)(dppe)_2]Cl were syn$ thesized, characterized and their reactions with acids studied. These complexes were prepared in a series of reactions starting with WCl_6 or $(MoCl_5)_2$ involving (i) introduction of the organohydrazido(2-) group (NNRR') using the corresponding hydrazine (R = R' = Me) or hydrazine hydrochloride (R = R' = Ph; R = Ph, R' = H or Me), and (ii) incorporation of phosphine ligands under reducing conditions. The particular product formed in the last step depended upon the reduction time. In almost all cases reaction of the complexes with acid (1 M HCl in Et_2O or H_2SO_4 in MeOH) resulted in the formation of some amine and a correspondingly smaller amount of ammonia. For example, the yields of aniline and ammonia when $[MCl(NNPh)(PMe_2Ph)_4]Cl$ reacted with H_2SO_4 in MeOH were ca 0.2 mol and ca 0.1 mol per mol of W, and 0.70 mol and 0.65 mol per mol of Mo, respectively. A comparison of acid reactions of organodiazenido and organohydrazido(2-)is made with those of unsubstituted hydrazido(2-) complexes prepared from coordinated dinitrogen. The crystal structure of reddish-brown [WCl₂(NN(H)Ph)(PMe₂Ph)₃] revealed a distorted octahedral complex in which the hydrazido(2-) moiety is *trans* to a chlorine atom and the hydrazido(2-) phenyl group is coplanar with the plane containing W, N, N and C(Ph) atoms. The second chlorine atom, *cis* to the hydrazido(2-) ligand, has a close intermolecular contact (2.62 Å) with the hydrazido(2-) hydrogen atom of a neighbouring molecule and close intramolecular contact (2.76 Å) with the endo o-phenyl hydrogen atom of the hydrazido(2-) ligand. Comparison of structural data with those for $[WCl_2(NNR_2)(PMe_2Ph)_3]$ (R₂ = Me₂ or Ph₂) indicates significant differences in W—N(1) and W—Cl(trans) distances between the dimethyl-, and the phenyl- and diphenylhydrazido(2-) complexes, respectively.

Generally, metal complexes containing an organohydrazido(2-) ligand that are prepared from an organohydrazine react with acid to generate the parent hydrazine rather than undergoing reduction to produce ammonia and the corresponding amine. There are two notable exceptions. First, the reduction of the aryldiimide complex, [Pt $(NHNC_6H_4F_{-p})Cl(PEt_3)_2]BF_4$, with dihydrogen

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over Pt, or aqueous dithionite, affords ammonia and *p*-fluoroaniline.¹ Second, the N-piperidino complex, which is prepared starting from *trans*-[Mo(N₂)₂(dppe)₂], reacts with HBr to yield piperidine and the imido complex [eq. (1)].² In a third example, in which no yield data are given, under N_2 . Solvents were thoroughly saturated with N_2 immediately prior to use by bubbling N_2 through the solvent. Quantitative analyses of aniline and ammonia were determined by the pentacyano-amminoferrate(III)⁹ and indophenol methods,¹⁰ respectively. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.



[MoO(NNMe₂)L₂] (L = C₉H₆NO, quinolin-8olate) reacts with anhydrous hydrogen halide to produce Me₂NH, Me₂NNH₂, and ammonia.³ In studies of related complexes Schrock *et al.* have shown that complexes such as [W(η^5 -C₅Me₅) Me₃(NNR₂)] undergo reactions that lead to N—N bond cleavage.⁴

In this paper, we report the synthesis of organohydrazido(2-) complexes including [MCl₂(NNR₂)] $(PR'_{3})_{3}$ and $[MCl_{2}(NNR_{2})(dppe)(PR'_{3})]$ where M = Mo or W; R = Me, Ph, H; $PR'_3 = PMe_2Ph$ or PPh_2Me ; $dppe = Ph_2PCH_2CH_2PPh_2$ together with phenyldiazenido complexes of the type $[MCl(NNPh)(PMe_2Ph)_4]$ (M = Mo, W). In many cases elemental analyses were poor, being particularly low in carbon. The new complexes reported in this paper react with acid to produce ammonia and the corresponding amine (e.g. eq. 2) in varying yields. Thus, they behave similarly to the structurally analogous unsubstituted hydrazido(2-) complexes of molybdenum and tungsten.5,6 Some of these results have been reported previously by us.^{7,8} We compare the reactivity of organodiazenido, organohydrazido(2-), and unsubstituted hydrazido(2-) complexes of molybdenum and tungsten with acids and comment on their methods of synthesis. The crystal structures [WCl₂(NNRR')(PMe₂Ph)₃], where of the R = R' = Me, R = R' = Ph; R = Ph, R' = H, arecompared.

EXPERIMENTAL

General procedures

All experimental procedures were conducted under strictly anaerobic conditions using either standard Schlenk techniques or a Vacuum Atmospheres Dribox filled with dinitrogen. All solvents were rigorously dried by heating at reflux over an appropriate drying agent, followed by distillation

Reagents and chemicals

Chemicals were purchased from commercial sources and used without further purification except for WCl₆ which was purified by sublimation. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. (Ph(Me)NNH₂·HCl,¹¹ [WCl₄(NNPh₂)],⁸ [WCl₂(NNPh₂)(PMe₂Ph)₃],⁸ and [MoCl₂(NNPh₂)(PMe₂Ph)₃]⁸ were prepared according to published procedures.

Instrumentation

The ¹H and ¹³C NMR spectra were obtained at room temperature on a General Electric Ω -300 operating at 300.52 MHz (1H) and 75.57 MHz (^{13}C) , and a General Electric Ω -500 operating at 500.10 MHz (¹H) and 125.76 MHz (¹³C). The proton-decoupled ³¹P NMR spectra were obtained at room temperature on a Varian VXR-200 operating at 80.961 MHz. Chemical shifts are referenced to Me₄Si (¹H, ¹³C) and PPh₃ (-5.8 ppm vs 85% $H_3PO_4 = 0.0$ ppm). Phosphorus atom assignments $[MCl_2(NNRR')(P_bMe_2Ph)]$ are as follows: $(P_aMe_2Ph)_2$, trans phosphorus atoms are P_a ; $[MCl_2(NNRR') (Ph_2P_aCH_2CH_2P_bPh_2) (P_cMe_2Ph)],$ P_a trans to P_c. FTIR spectra were recorded using an Analect RFX-65 FTIR spectrometer. Cyclic voltammetry (CV) was performed at room temperature at a scan rate of 50 mV/s in a twocompartment three-electrode cell. The working electrode was a platinum wire, which was probed by a Luggin capillary connected to as silver pseudoreference electrode; a tungsten auxiliary electrode was employed. The electrolyte was 0.2 M [Bu₄N][BF₄] in dry distilled THF. Potentials quoted are referenced to the ferrocenium/ferrocene (Fc^+/Fc) couple = 0.0 V (0.535 V vs SCE in this electrolyte).

$[WCl_4(NNMe_2)]$

1,1-Dimethylhydrazine (0.40 cm³, 5.20 mmol, d = 0.791 g/cm³) was added to WCl₆ (2.10 g, 5.29 mmol) in a Schlenk flask cooled to -78° C. Dichloromethane (30 cm³) was added and the mixture stirred (0.08 h). Solvent was removed *in vacuo* while the mixture warmed to room temperature. After drying (0.5 h) *in vacuo*, pentane (50 cm³) was added and the mixture stirred (0.2 h). The solid product was filtered off, washed with pentane (2 × 5 cm³), and dried *in vacuo*. The yield of burgundy-colored product was 1.79 g (88%).

[WCl₄(NN(Me)Ph)] and [WCl₄(NN(H)Ph)]

These complexes were prepared according to the previous procedure, using the corresponding hydrazine hydrochloride salt, as maroon (92% yield) and rust-brown (86% yield) colored complexes, respectively.

[WCl₂(NNMe₂)(PMe₂Ph)₃]

A mixture of 1% sodium amalgam (0.75 g, 32 mmol Na), THF (30 cm³), and PMe₂Ph (1.30 g, 9.4 mmol) was stirred (0.03 h). $[WCl_4(NNMe_2)]$ (1.20 g, 3.13 mmol) was then added and the whole mixture stirred (0.75 h). The solution was decanted from the amalgam and filtered through Celite. The volume of solution was reduced to $ca \ 15 \ cm^3$ in vacuo before pentane (40 cm³) was added to precipitate the product. The orange product was filtered off, washed with pentane $(3 \times 10 \text{ cm}^3)$, and dried in vacuo. The yield of product was 65% (1.45 g, 2.03 mmol). Found: C, 39.4; H, 5.4; N, 3.3. Calc. for $C_{26}H_{39}Cl_2N_2P_3W$; C, 43.0; H, 5.4; N, 3.9%. ³¹P NMR (CD₂Cl₂): δ – 14.3 (s, 2, J_{PW} = 296 Hz, P_a), -13.3 (s, 1, $J_{PW} = 380$ Hz, P_b). ¹H NMR $(CD_2Cl_2): \delta 1.39 \ (d, 6, J_{PH} = 8.3 \ Hz, PMe), 1.71$ $(t, 6, J_{PH} = 3.6 \text{ Hz}, PMe), 1.82 (t, 6, J_{PH} = 3.7)$ Hz, PMe), 2.54 (s, 6, NMe), 6.82 (t, 2, J = 8.6Hz, Ph), 7.07 (t, 2, J = 7.3)Hz, Ph), 7.16 (t, 1, J = 6.9 Hz, Ph), 7.34-7.52 (m, 10, Ph). ¹³C NMR (CD₂Cl₂): δ 13.44 (t, J_{PC} = 13.2 Hz, PMe), 17.63 (t, $J_{PC} = 13.2$ Hz, PMe), 23.08 (d, $J_{PC} = 31.9$ Hz, PMe), 42.43 (s, NMe), 128.14 – 130.63 (m, Ph). CV: pseudo-reversible one-electron oxidation wave at -0.61 V and irreversible reduction wave at -2.0V.

[WCl₂(NN(Me)Ph)(PMe₂Ph)₃]

This green-brown complex was prepared in 69% yield according to the previous procedure. Found : C, 45.2; H, 5.1; N, 3.2. Calc. for $C_{31}H_{41}Cl_2N_2P_3W$:

C, 47.2; H, 5.2; N, 3.5%. ³¹P NMR (THF): $\delta - 15.4$ (s, 2, $J_{PW} = 290$ Hz, P_a), -15.8 (s, 1, $J_{PW} = 361$ Hz, P_b). ¹H NMR (CD₂Cl₂): δ 1.59 (d, 6, $J_{PH} = 8.8$ Hz, PMe), 1.71 (t, 6, $J_{PH} = 3.7$ Hz, PMe), 1.79 (t, 6, $J_{PH} = 3.6$ Hz, PMe), 2.31 (s, 3, NMe), 6.30 (t, 2, J = 8.2 Hz, Ph), 6.92 (t, 1, J = 6.8 Hz, Ph), 6.98 (t, 2, J = 7.3 Hz, Ph), 7.16 (t, 1, J = 7.4 Hz, Ph), 7.15–7.39 (m, 14, Ph). ¹³C NMR (CD₂Cl₂): δ 12.29 (t, $J_{PC} = 13.2$ Hz, PMe), 18.11 (t, $J_{PC} = 13.2$ Hz, PMe), 24.03 (d, $J_{PC} = 31.9$ Hz, PMe), 36.16 (s, NMe), 114.03 (s, Ph), 121.23 (s, Ph), 128.39–130.88 (m, Ph), 143.66 (d, $J_{PC} = 24.2$ Hz, Ph).

$[WCl_2(NN(H)Ph)(PMe_2Ph)_3]$

This rust-colored complex was prepared in 75% yield according to the previous procedure. It is very important not to allow the reduction step to continue for more than 0.17 h at room temperature. ³¹P NMR (CD₂Cl₂): δ -15.3 (s, 1, J_{PW} = 373 Hz, P_b), -16.4 (s, 2, $J_{PW} = 292$ Hz, P_a). ¹H NMR (CD₂Cl₂): δ 1.52 (d, 6, $J_{PH} = 8.1$ Hz, PMe), 1.79 (s, 6, PMe), 1.87 (s, 6, PMe), 4.85 (s, 1, NH), 6.20 (t, 2, J = 8.0(d, 2, J = 7.6 Hz, Ph),6.88 Hz, Ph), 6.80 (t, 1, J = 7.4 Hz, Ph), 7.06 (t, 2, J = 7.5 Hz, Ph),7.21–7.37 (m, 13, Ph). ¹³C NMR (CD₂Cl₂) : δ 12.67 (s, PMe), 18.12 (bs, PMe), 22.71 (bs, PMe), 112.20 (s, Ph), 121.33 (s, Ph), 128.27 (s, Ph), 128.61–130.53 (m, Ph), 143.37 (bs, Ph). CV: Pseudo-reversible oxidation at 0.40 V and an irreversible reduction wave at -1.96 V.

$[WCl(NNPh)(PMe_2Ph)_4]$

This dark yellow complex was prepared in 69% vield according to the previous procedure using four rather than three equivalents of PMe₂Ph and allowing the reduction step to continue for 0.75-1.0 h. Found : C, 51.0; H, 5.6; N, 3.0; Cl, 4.2. Calc. for C₃₈H₄₉ClN₂P₄W: C, 52.0; H, 5.6; N, 3.2; Cl, 4.0%. ³¹P NMR (CD₂Cl₂): δ -21.8 (s, J_{PW} = 290 Hz). ¹H NMR (CD₂Cl₂): δ 1.32 (d, 6, $J_{PH} = 2.5$ Hz, PMe), 1.60 (s, 10, PMe), 1.69 (d, 6, $J_{PH} = 13$ Hz, PMe), 1.97 (d, $2, J_{PH} = 11.5$ Hz, PMe), 6.57 (bt, 2, J = 5.3, Ph), 6.89 (d, 2, J = 7.3 Hz, Ph),7.09–7.79 (m, 22, Ph). ¹³C NMR (CD₂Cl₂): δ 13.68 $(d, J_{PC} = 14.8 \text{ Hz}, PMe), 17.36 (s, PMe), 17.93$ (s, PMe), 128.50-132.15 (m, Ph). CV: irreversible oxidation wave at -0.17 V and no reduction waves before reduction of solvent.

[WCl₃(NNPh₂)(dppe)] and [WCl₃(NN(Me)Ph) (dppe)]

To a mixture of zinc (0.94 g, 14 mmol), dppe (1.14 g, 2.85 mmol), and CH_2Cl_2 (30 cm³) was

added [WCl₄(NNPh₂)] (1.46 g, 2.87 mmol). After stirring the mixture (0.5 h), the suspension was poured from the zinc, and pentane (75 cm³) added to complete precipitation of product. The solid was filtered off, washed with pentane (2×10 cm³), and dried *in vacuo*. The yellow product was isolated in almost quantitative yield. The brown methylphenylhydrazido(2-) complex was prepared similarly.

[WCl₂(NNPh₂)(dppe)(PMe₂Ph)]

A mixture of PMe₂Ph (0.157 g, 1.14 mmol), THF (30 cm³), and a ten-fold excess of 1% sodium amalgam was stirred (0.03 h) before the addition of [WCl₃(NNPh₂)(dppe)] (1.00 g, 1.15 mmol). After stirring (0.17 h), the solution was decanted from the amalgam and filtered through Celite. The solution volume was reduced to 10–15 cm³ before pentane (60 cm³) was added to precipitate the product. The tan solid was filtered off, washed with pentane $(2 \times 10 \text{ cm}^3)$, and dried in vacuo. The product was obtained in 82% yield (0.916 g, 0.941 mmol). ³¹P NMR (THF): δ 44.34 (d, 1, $J_{PaPb} = 25.0$ Hz, $J_{PbW} = 352$ Hz, P_b), 26.20 (dd, 1, $J_{PaPc} = 200$ $H_z, J_{PaW} = 288 H_z, P_a) - 19.82 (d, 1, J_{PcW} = 310)$ Hz, P_c). ¹H NMR (CD₂Cl₂): δ 1.46 (d, 3, J_{PH} = 8.5 Hz, PMe), 1.90 (d, $3, J_{PH} = 8.5$ Hz, PMe), 2.41 (m, 2, PCH₂), 2.88 (m, 1, PCH₂), 3.25 (m, 1, PCH₂), 6.68–7.88 (m, 35, Ph). ¹³C NMR (CD₂Cl₂): δ 14.60 (d, J = 25.9) $(d, J_{PC} = 29.6)$ Hz, PMe), 15.50 Hz, PMe), 29.42 (dd, $J_{PC} = 6.5$ Hz, $J_{PC} = 30.5$ Hz, PCH₂), 36.41 (dd, $J_{PC} = 7.4$ Hz, $J_{PC} = 31.4$ Hz, PCH₂), 121.4–143.6 (m, Ph).

$[WCl(NNPh_2)(dppe)_2]Cl \quad and \quad [WCl(NN(Me) Ph)(dppe)_2]Cl$

These complexes were prepared similarly starting with [WCl₃(NNPh₂)(dppe)] and [WCl₃(NN(Me) Ph)(dppe)] using one equivalent of dppe and allowing the reduction to occur for 1.0-1.5 h, respectively. The yield of [WCl(NNPh₂)(dppe)₂]Cl was 26% (0.3971 g, 0.322 mmol). ³¹P NMR (THF): δ 43.32 (s, $J_{PW} = 234$ Hz). ¹H NMR (CD₂Cl₂) : δ 2.45 (bs, 4, PCH₂), $(bs, 4, PCH_2),$ 2.83 7.01-7.73 ¹³C NMR (CD_2Cl_2) : (m, 50, Ph). δ 15.08 $(dd, J = 6.29 Hz, J = 23.89 Hz, PCH_2),$ 29.95 37.25 $(dd, J = 2.10 \quad Hz, J = 6.30$ $Hz, PCH_2),$ $(dd, J = 2.10 Hz, J = 6.30 Hz, PCH_2), 121.6-143.8$ (m, Ph). $[WCl(NN(Me)Ph)(dppe)_2]Cl; {}^{31}P NMR$ (THF): δ 47.36 (s, $J_{PW} = 320$ Hz). ¹H NMR $(CD_2Cl_2): \delta 2.33 \text{ (m, 11, NMe, PCH}_2), 7.01-7.24$ (m, ~45, Ph). ¹³C NMR (CD₂Cl₂): δ 31.77 Hz, NMe, PCH₂), 125.50-133.51 (t, J = 20.35)(m, Ph), 138.60 (t, J = 7.42 Hz, Ph).

[MoCl₃(NNMe₂)], [MoCl₃(NNPh₂)], and [MoCl₃ (NN(H)Ph)]

These complexes were prepared in almost quantitative yield according to the method used to synthesize the corresponding $[WCl_4(NNR_2)]$ complexes beginning with $(MoCl_5)_2$. $[MoCl_3(NNMe_2)]$ and $[MoCl_3(NNPh_2)]$ are purple and $[MoCl_3(NN(H)Ph)]$ is black. Found: C, 35.8; H, 2.7; N, 6.7; Cl, 27.4. Calc. for $C_{12}H_{10}Cl_3N_2Mo$: C, 37.4; H, 2.6; N, 7.3; Cl, 27.3%.

$[MoCl_2(NNMe_2)(PMe_2Ph)_3]$

This green-brown complex was prepared in 55% yield similarly to the tungsten analog with a reduction time of 0.17 h using 1% sodium amalgam (1.0 g, 43 mmol Na), PMe₂Ph (1.25 g, 9.0 mmol), THF (50 cm³), and [MoCl₃(NNMe₂)] (0.887 g, 3.00 mmol). ³¹P NMR (CD₂Cl₂) : δ 14.77 (t, 1, J_{PP} = 16.2 Hz, P_b), 4.16 (d, 2, P_a). ¹H NMR (CD₂Cl₂): δ 1.26 $(d, 6, J_{PH} = 8.1 \text{ Hz}, PMe), 1.63 (t, 6, J_{PH} = 3.5)$ Hz, PMe), 1.74 (t, 6, $J_{PH} = 3.6$ Hz, PMe), 2.58 $(s, 6, NMe), 6.82 (t, 2, J_{PH} = 8.8 Hz, Ph), 7.09$ $(t, 2, J_{PH} = 7.5 \text{ Hz, Ph}), 7.20 (t, 1, J_{PH} = 7.39)$ Hz, Ph), 7.34–7.51 (m, 10, Ph). ${}^{13}C$ NMR (CD₂Cl₂): δ 12.35 (t, J_{PC} = 11.1 Hz, PMe), 15.97 (t, J_{PC} = 12.0 Hz, PMe), 19.04 (d, $J_{PC} = 25.9$ Hz, PMe), 41.86 (s, NMe), 128.4–131.0 (m, Ph). CV: pseudo-reversible oxidation wave at -0.26 V, pseudo-reversible reduction wave at -1.38 V.

$[MoCl(NNPh)(PMe_2Ph)_4]$

This brown-black complex was prepared as for the tungsten analogue using 1 h reduction time. ³¹P NMR (CD₂Cl₂): δ 30.3 (s). ¹H NMR (CD₂Cl₂): 1.30 (d, 14, J_{PH} = 2.7 Hz, PMe), 1.67 (d, 10, J_{PH} = 12.9 Hz, PMe), 6.65-7.72 (m, 25, Ph).

[MoCl₃(NNPh₂)(dppe)]

This orange compound was prepared similarly to its tungsten analog in quantitative yield.

[MoCl₂(NNPh₂)(dppe)(PMe₂Ph)]

This complex was prepared similarly to its tungsten analog in 68% yield with a 0.17 h reduction time. ³¹P NMR (THF): δ 60.20 (dd, 1, $J_{PaPb} = 6.4$ Hz, $J_{PbPc} = 16.0$ Hz, P_b), 35.09 (dd, 1, $J_{PaPc} = 208$ Hz, P_a), 0.90 (dd, 1, P_c). ¹H NMR (CDCl₃): δ 1.04 (d, 3, $J_{PH} = 7.7$ Hz, PMe), 1.68 (d, 3, $J_{PH} = 6.5$ Hz, PMe), 2.03 (m, 1, PCH₂), 2.42 (m, 1, PCH₂), 2.73 (m, 1, PCH₂), 3.16 (m, 1, PCH₂), 6.52–7.71 (m, Ph).

[MoCl(NNPh₂)(dppe)₂]Cl

This complex was prepared similarly to its tungsten analog after 1 h in 31% yield (based on [MoCl₃(NNPh₂)(dppe)] used). ³¹P NMR (CD₂Cl₂): δ 52.85 (s). ¹H NMR (CD₂Cl₂): δ , 2.45 (m, 4, PCH₂), 2.91 (m, 4, PCH₂), 6.99–7.87 (m, ~ 50, Ph). ¹³C NMR (CD₂Cl₂): δ 30.33 (quin, $J_{PC} = 9.3$ Hz, PCH₂) 128.07–134.26 (m, Ph), 136.69 (m, Ph), 138.37 (m, Ph).

Single-crystal X-ray structure determination

Small (ca 0.025 mm³) reddish-brown prisms of $[WCl_2(NN(H)Ph)(PMe_2Ph)_3]$ were mounted in sealed thin-walled capillaries on a Siemens P4 diffractometer using graphite-monochromated Mo- K_{α} radiation. Substantial crystal decay was observed during data collection, so that three crystals were ultimately used to collect a complete merged data set; considerable overlap amongst the individual crystal data sets ensured that accurate inter-set scale factors could be calculated. A precise unit cell, based on the setting angles of 28 carefully centered reflections in the range 19.5–20° 2θ was refined. The data were collected at room temperature (~25°C) using θ scans to a maximum 2θ value of 50°. Three standard reflections were measured at the beginning of the data collection, and then again after each 97 collected reflections. The orientation matrix was re-determined after every 500 reflections. Due to the crystal decay, the crystal was replaced when the intensity of the standard reflections had dropped to 75–80% of its initial value. After correction for Lorentz and polarization effects, a total of 7902 reflections were collected in a single data set. Of these, 191 were rejected as violating space-group absences. Merging resulted in 5995 unique reflections, of which 3846 had $F > 4\sigma(F)$. The merging R factor was 0.044.

The crystal is monoclinic with space group $P2_1/n$ (14), empirical formula $C_{30}H_{39}Cl_2N_2P_3W$, $M_r = 775.3$, a = 12.1120(10), b = 23.754(2), c = 13.193(2) Å, $\beta = 109.150(10)^\circ$, V = 3585.7(7)Å³, Z = 4, $D_c = 1.436$ Mg/m³, $\mu = 3.525$ mm⁻¹, F(000) = 1544.

The structure was solved by Patterson methods. An attempt was made simultaneously to refine the positions and anisotropic ADPs of all heavy atoms, however it was observed that the resulting interatomic bond lengths and angles in the phenyl groups were chemically unreasonable. To remedy this, a model restraining the interatomic distances of phenyl-ring carbon atoms (1.385 Å for nearest and 2.399 Å for next-nearest neighbours with weights of 0.001 Å and 0.002 Å, respectively) was

used. These values were determined by analysis of structures in the Cambridge Crystallographic Database. Each set of six phenyl-ring carbon atoms was constrained to have the same isotropic ADP, and the phenyl hydrogen atoms were constrained to a riding model with isotropic ADP equal to 1.2 times the ADP of the corresponding carbon atom. All other heavy atoms (W, P, Cl, N and methyl C) were refined as individual atoms with anisotropic ADPs, and all other hydrogen atoms were refined using a riding model with isotropic ADP = 0.08 Å^{-2} . No absorption correction was applied. The final cycles of least-squares refinement were performed using modified Poisson weighting and 203 refinable parameters. The final statistical parameters were: R = 0.064, wR = 0.085, S = 1.56. Selected interatomic distances and angles are found in Table 1. For reference, it might be noted that the original model (free, anisotropic heavy atoms, riding H) had 343 parameters, R = 0.061, wR = 0.078, S = 1.47. A Hamilton test is, in this case, necessary, as this model resulted in a chemically unreasonable model. However the moderate increase in R, wRand S given the large decrease (41%) in refinable parameters is satisfactory. Full crystal data, positional parameters, hydrogen atom coordinates and thermal parameters are available from the Cambridge Crystallographic Data Center.

RESULTS AND DISCUSSION

Synthesis of [WCl₄(NNR₂)] and [MoCl₃(NNR₂)] complexes

The simple hydrazido(2-) complexes [WCl₄ (NNR₂)] and [MoCl₃(NNR₂)] were readily prepared (eq. 3) by reacting either good quality WCl₆ or (MoCl₅)₂ with the

WCl₆ + Ph₂NNH₂ · HCl
$$\xrightarrow{CH_2Cl_2}_{-78 \cdot C}$$

[WCl₄(NNPh₂)] + 3HCl (3)

corresponding hydrazine (R = Me) or hydrazine hydrochloride salt (R = Ph) in CH_2Cl_2 at $-78^{\circ}C$ following a procedure first reported by Dilworth and Morton.¹² The reactions were carried out in the correct stoichiometry in order to avoid the formation of any bis(hydrazido) complex. Both [MCl₄(NN(H)Ph)] and [M(NN(Me)Ph)] were made using the corresponding hydrazine hydrochloride salt since reactions using the free hydrazine afforded a mixture of products. The tungsten and molybdenum complexes have characteristic colors and were stored for long periods of time in the

	Ι	II	III
W-N(1)	1.757(11)	1.761(8)	1.851(5)
N(1) - N(2)	1.348(17)	1.36(1)	1.385(8)
W	2.476(4)	2.486(3)	2.625(2)
W - P(1)	2.489(5)	2.517(3)	2.442(2)
W - P(2)	2.495(5)	2.506(3)	2.422(2)
W-P(3)	2.467(4)	2.481(3)	2.391(2)
W-Cl(1)	2.532(4)	2.497(3)	2.481(2)
N(2)C(25)	1.380(17)		
N(2)H	0.97		
Cl(2)WN(1)	176.1(4)	W—N(1)—N(2)	178.5(12)
N(1) - N(2) - C(25)	124.3(12)	Cl(1) - W - Cl(2)	85.1(1)
Cl(1) - W - N(1)	98.7(4)	P(1)-W-Cl(2)	90.9(1)
P(1) - W - N(1)	95.4(4)		

Table 1. Selected bond lengths (Å) for $[WCl_2(NN(H)Ph)(PMe_2Ph)_3]$ (I), $[WCl_2(NNPh_2)(PMe_2Ph)_3]$, (II) and $[WCl_2(NNMe_2)(PMe_2Ph)_3]$ (III) and bond angles (°) for $[WCl_2(NN(H)Ph)(PMe_2Ph)_3]$ (I)

absence of air and moisture without visible sign of decomposition except for [WCl₄NN(H)Ph].

Synthesis and characterization of [MCl₂(NNR₂) (PR'₃)₃] and [MCl₂(NNR₂)(dppe)(PMe₂Ph)₃] complexes

Successful incorporation of phosphine ligands into the coordination sphere during reduction required careful attention to reaction stoichiometry and time (eq. 4).

$$[WCl_4(NNPh_2)] + 3PMe_2Ph + 2Na/Hg \xrightarrow{\text{IHF}} [WCl_2(NNPh_2)(PMe_2Ph)_3] + 2NaCl \quad (4)$$

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Optimum times for reduction using excess sodium amalgam, which was judged to be the most suitable reducing agent, were determined by monitoring the reaction by ³¹P NMR spectroscopy. Excess zinc performed the reduction but too slowly to be useful. During the 45-60 min of the reduction reaction of [WCl₄(NNPh₂)] with three equivalents of PMe₂Ph in THF solution, two singlets due to $[WCl_2(NNPh_2)]$ (PMe₂Ph)₃] began to appear in the ³¹P NMR spectrum. Coupling between phosphorus atoms was not observed in any of the diorganohydrazido(2-)tungsten complexes containing three PMe₂Ph ligands. After an hour, the intensity of these resonances decreased while the resonance due to free PMe_2Ph at -47.1 ppm increased until it was the only resonance visible in the spectrum. Away from the amalgam, $[WCl_2(NNR_2)(PMe_2Ph)_3]$ complexes were stable in solution. This is in contrast to analogous PPh₂Me complexes which were not only susceptible to further reduction but were also unstable in solution away from the amalgam. Thus, when freshly prepared solutions of $[WCl_2(NNR_2)$ $(PPh_2Me)_3]$ in THF were decanted from the amalgam, resonances due to product continued to decrease while that for free PPh₂Me increased. No other NMR-active phosphine-containing product was detected in solution.

In an effort to increase the stability of the complexes, particularly following the loss of one phosphine ligand, complexes containing a dppe ligand were synthesized. First, [WCl₃(NNR₂)(dppe)] was prepared by reducing a mixture of [WCl₄(NNR₂)] and dppe in CH_2Cl_2 with zinc. Second, a mixture of [WCl₃(NNR₂)(dppe)] and PR₃ was reduced with sodium amalgam. Solutions of complexes containing PMe₂Ph were stable away from the amalgam but those complexes containing PPh₂Me were unstable due to dissociation of PPh₂Me. When [WCl₂(NNPh₂)(dppe)(PPh₂Me)] decomposed in solution, resonances due to free PPh2Me and [WCl(NNPh₂)(dppe)₂]Cl were observed in the ³¹P NMR spectrum. A similar complex was prepared independently: reduction of a mixture of [WCl₃(NN(Me)Ph)(dppe)] and dppe in THF with excess sodium amalgam was monitored by ³¹P NMR spectroscopy. During the early part of the reaction, resonances were observed that could be attributed to a species containing three coordinated phosphorus atoms such as $[WCl_2(NN(Me)Ph)(\eta^2$ dppe)(η^1 -dppe)]. Gradually, these three resonances gave way to a single resonance, with tungsten satellites, due to [WCl(NN(Me)Ph)(dppe)₂]Cl. In a further study, [WCl₂(NNPh₂)(dppe)(PPh₂Me)] was



-78°C. (ii) $3PMe_2Ph$, Na/Hg, THF (R = R' = Ph; R = R' = Me; R = Ph, R' = Me or H). (iii) dppe, Zn, CH_2Cl_2 (R = R' = Ph; R = Ph, R' = Me). (iv) PMe_2Ph , Na/Hg, THF (R = R' = Ph). (v) dppe, Na/Hg, THF (R = R' = Ph; R = Ph, R' = Me). (vi) $4PMe_2Ph$, Na/Hg, THF (R = Ph, R' = H). (v) PMe_2Ph , Na/Hg, THF (R = Ph, R' = H).

prepared to the point of the Celite filtration and then one equivalent of PMe_2Ph was added to the THF solution. Monitoring this mixture by ³¹P NMR spectroscopy showed the peaks due to the PPh_2Me complex disappearing, and a new stable product forming, [WCl₂(NNPh₂)(dppe)(PMe₂Ph)]. This supported the hypothesis that loss of a phosphine is the first step in the further reaction of these complexes and occurs prior to electron transfer. These same events occur with the (NNH₂) complexes.¹³

The room temperature preparation of the analogous molybdenum complexes $[MoCl_2(NNR_2)$ $(PR_3)_3]$ required much shorter reduction times, about 0.17 h. Molybdenum complexes were less stable in all aspects than their tungsten analogs.

Synthesis and characterization of [MCl₂(NN (H)Ph)(PMe₂Ph)₃] and [MCl(NNPh)(PMe₂Ph)₄]

The reduction of a mixture of $[WCl_4(NN(H)Ph)]$ and three equivalents of PMe_2Ph in THF with excess sodium amalgam was monitored by ³¹P NMR spectroscopy. After *ca* 0.17 h, three single resonances were observed, one due to free PMe_2Ph and the other two, with tungsten satellites, assigned to $[WCl_2(NN(H)Ph)(PMe_2Ph)_3]$. At this time, the hydrazido(2–) complex was isolated in 75% yield. The proton on the nitrogen was observed at 5.3 ppm in the ¹H NMR spectrum. This resonance disappeared when D_2O was added. The identity of this complex was established by an X-ray crystal structure determination (vide infra). The hydrazido(2-) complex slowly decomposed in the solid state when stored under dinitrogen at room temperature in the dark. When reduction was carried out for 0.25 h, a single new resonance began to appear as the major peak as the others decreased in intensity, until after 0.75 h only the new single resonance with tungsten satellites was present. The ratio of Ph (25) to Me (24) protons in the ¹H NMR spectrum supports the assignment of this as the diazenido complex [WCl(NNPh)(PMe₂Ph)₄] with four phosphine ligands. No evidence of a proton bound to the nitrogen atom was available from either the ¹H NMR or FTIR spectra. This complex was also prepared directly by reducing a mixture of $[WCl_4(NN(H)Ph)]$ and four equivalents of PMe₂Ph in THF for 1 h. The phenyldiazenido complex is rapidly protonated to form [WCl₂(NN(H)Ph) (PMe₂Ph)₃] with loss of a phosphine. There is no formal oxidation state change upon converting the hydrazido(2-) complex into the diazenido complex. Thus, the hydrazido(2-) complex underwent dehydrohalogenation with addition of a fourth phosphine ligand. In the reaction with only three equivalents of phosphine, acquisition of a fourth phosphine comes at the expense of a preexisting hydrazido(2-) complex which itself does not produce a complex with resonances observable in the ³¹P NMR spectrum. It appears to be a general observation among the complexes reported in this paper, that the phosphine ligands are labile and once dissociated generate complexes that are not observed in either the ¹H or ³¹P NMR spectrum, possibly because the coordinatively unsaturated complexes undergo redox reactions. The exceptions to this observation are the complexes with two dppe ligands.

Reduction of a mixture of $[MoCl_3(NN(H)Ph)]$ and PMe₂Ph resulted in the isolation of $[MoCl (NNPh)(PMe_2Ph)_4]$ in low yield. Although resonances attributable to a species such as $[MoCl_2(NN(H)Ph)(PMe_2Ph)_3]$ could be seen in the ³¹P NMR spectrum, its lifetime was considerably shorter than the analogous tungsten complex.

Reactions with acid

The tungsten complexes $[WCl_2(NNR_2)(PMe_2 Ph)_3](R_2 = Me_2 \text{ or } Ph_2)$ reacted with a variety of acids, such as 1.0 M HCl in ether, aqueous HBr, or triflic acid, to generate the corresponding amine and ammonia (eq. 2). These results have been reported previously; *ca* 0.6 mol of amine and 0.25 mol of ammonia per mol of tungsten.^{7.8} The results demonstrate that these organohydrazido(2 –) complexes are behaving similarly to unsubstituted hydrazido(2 –) analogs that have been shown to produce ammonia. The corresponding molyddenum complexes reacted with acid but produced only a trace of ammonia and amine.

Both $[WCl_2(NN(H)Ph)(PMe_2Ph)_3]$ and $[WCl (NNPh)(PMe_2Ph)_4]$ reacted with sulfuric acid in methanol to produce less than 0.2 mol of aniline and *ca* 0.1 mol of ammonia per mol of tungsten. However, under the same conditions [MoCl (NNPh)(PMe_2Ph)_4] produced 0.70 mol of aniline and 0.65 mol ammonia per mol of molybdenum, respectively. With water alone, the phenyldiazenido complex (dissolved in CH₂Cl₂) produced 0.25 and 0.20 mol of aniline and ammonia, respectively.

Comparison of the reactions of organodiazenido, organohydrazido(2-), and unsubstituted hydrazido(2-) complexes with acids

Successful protonation of coordinated dinitrogen requires a ready source of electrons. Electrons necessary for the formation of the initial N—H bonds come from the metal or metals to which dinitrogen is bonded. Successive electrons may come from either the same metal,⁵ from disproportionation of an intermediate,¹³ an added chemical reductant,¹⁴⁻¹⁶ or an electrode.¹⁷ Formally, two electrons are required for the conversion of the hydrazido(2–) moiety into two mol of ammonia, or one mol of amine and ammonia, respectively. In

a few cases, which depend upon solvent and acid, two mol of ammonia are produced per mol of hydrazido(2-) complex.⁵ In most cases, the yield of ammonia is significantly less than 100%. We have shown that some unsubstituted hydrazido(2-)complexes of molybdenum form ammonia as a result of disproportionation $N_2 + 2NH_3 + 2e^{-}$.^{13,18} $(2{NNH_2^{2-}}+2H^+)$ \rightarrow Although the diorganohydrazido(2-) complexes of the type reported in this paper are isoelectronic and isostructural with the unsubstituted analogs, the same type of disproportionation of the (NNR_2) moiety is unlikely because the N-C bond is significantly less labile than the N-H bond.

Comments on the synthesis of diazenido and hydrazido(2-) complexes

A wide variety of alkyldiazenido, alkylhydrazido(2-) and dialkylhydrazido(2-) complexes of molybdenum and tungsten with two bidentate ligands such as dppe can be prepared directly from the corresponding bis(dinitrogen) complex by alkylation or alkylation followed by protonation.^{19,20} Generally, these reactions are limited to bromo- and iodoalkanes.²¹ Direct arylation of these same bis(dinitrogen) complexes of molybdenum and tungsten has been demonstrated.²²⁻²⁵ These same reactions do not occur with bis(dinitrogen) complexes containing monodentate phosphine ligands. It is now possible using the synthetic pathways described here to prepare a wider variety of aryldiazenido and dialkyl-, alkylaryl- and diarylhydrazido(2-) complexes of molybdenum and tungsten with bidentate and small monodentate phosphine ligands.

Crystal structures of [WCl₂(NNRR')(PMe₂Ph)₃]

Crystals of $[WCl_2(NN(H)Ph(PMe_2Ph)_3]$ were obtained from a THF solution following the addition of pentane. The structure (Fig. 1) shows a short W—N(1) distance and a N(1)—N(2) distance that is intermediate between calculated single and double bond distances, indicating a high degree of delocalization and significant multiple bond character throughout the W-N(1)-N(2) moiety, like other hydrazido(2-) complexes of tungsten (and molybdenum).²⁴ In addition, the hydrazido phenyl group is coplanar with the plane containing W, N(1), N(2) and C(25), thus maximizing the degree of conjugation between the two units. The phenyl ring is also coplanar with the plane containing W, N(1), Cl(1), Cl(2), and P(3). As a result the endo o-phenyl proton is only 2.76 Å from Cl(1), a distance less than the sum of the van der Waal



Fig. 1. ORTEP view of the structure of $[WCl_2(NN(H)Ph)(PMe_2Ph)_3].$

radii.25 This chlorine atom is also involved in hydrogen bonding to the hydrazido hydrogen atom (2.62 Å) of a neighbouring molecule. A list of common bond lengths of the three hydrazido(2-) complexes are found in Table 1. In all three structures, the orientation of groups on the phosphorus atoms are different. Likewise, the orientation of the phenyl group in the (NN(H)Ph) complex is different from both of those in the (NNPh₂) complex. As noted previously,^{7,8} there are significant bond length differences between the dimethyl- and diphenylhydrazido(2-) complexes, however, the phenyland diphenylhydrazido(2-) complexes are very similar. Within the N-N-W-Cl_{trans} unit the N—N distances are similar in all three complexes but both the W—N(1) and W—Cl(2) bonds are significantly longer and the three W-P distances are all correspondingly shorter in the dimethylhydrazido(2-) complex. In the absence of any clear steric factors, one explanation for these observations is based upon the two possible resonance forms, A and B, that have been proposed for hydrazido complexes. In the phenyl- and diphenylhydrazido complexes, in which the W-N is shorter, tungsten is

$$\ddot{W}^{II} = N = NR_2$$
 (A) $\ddot{W}^{IV} = N - \ddot{N}R_2$ (B)

in a higher oxidation state as a result of stronger π bonding with N(1), resonance form **B**, which contributes to a shorter W—Cl(1) distance. In addition, delocalization of the lone pair of electrons on the terminal nitrogen over the phenyl ring will favor resonance form **B**. In the dimethylhydrazido complex, the longer W—N(1) distance suggests less π -bonding such that resonance form **A** may be more appropriate. As N(1) and Cl(1) move further from tungsten, the W—P distances become significantly shorter in the dimethylhydrazido complex (see Table 1). Similar structural changes were observed when the diazenido complex [MoI(NNoctyl-n)(dppe)₂] was protonated to form the hydrazido complex [MoI(NN(H)octyl-n)(dppe)₂]I: Mo—I and Mo—N(1) decreased from 2.882(2) and 1.850(12) to 2.819(1) and 1.801(5) Å, respectively, while the Mo—P_(av) increased from 2.514(3) to 2.542(2), respectively.²⁶ The bond-length differences among the hydrazido complexes have not resulted in any noticeable differences in chemical behavior.

CONCLUSION

The synthesis of a variety of phenyldiazenido, phenylhydrazido(2–), dimethyl-, diphenyl-, and methylphenylhydrazido(2–) complexes of molybdenum and tungsten with organophosphine ligands starting from WCl₆ or (MoCl₅)₂ have been reported. None of these complexes can be made by the alkylation or arylation of the corresponding bis(dinitrogen) complexes. It has been shown that the organohydrazido(2–) complexes react with acid to form an amine and ammonia, just as the unsubstituted hydrazido(2–) complexes react to form ammonia, although the mechanisms may be different. In both series of reactions, the presence of a labile ligand (PR₃), is required for the reaction to occur.

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