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DIAZOALKANE COMPLEXES OF TUNGSTEN FROM THE CONDENSATION OF HYDRAZIDO COMPLEXES WITH KETONES *

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Summary

Hydrazido(2—) and hydrazido(1—) complexes of tungsten condense with ketones, R^1R^2CO, in the presence of catalytic amounts of acid to yield complexes containing the groups $W{=}N{-}N{=}CR^1R^2$ and $W{-}NH{-}N{=}CR^1R^2$ respectively. The other ligands are halide ions and monotertiary phosphines. These new complexes yield secondary amines and ammonia on reduction with $LiAlH_4$; acids produce nitrogen-free tungsten materials, hydrazine and azines.

Introduction

We have recently shown [1,2] that alkyl bromides, RBr, react with the bis-(dinitrogen) complexes $[M(N_2)_2(dppe)_2]$ (M = Mo or W, dppe = 1,2-bis(diphenylphosphino)ethane) in benzene solution to yield diazenido complexes $[MBr(N_2R)(dppe)_2]$, and that *gem*-dibromides $R^1R^2CBr_2$ and the bis(dinitrogen) complexes yield diazoalkane complexes $[MBr(N_2CR^1R^2)(dppe)_2]^+$ [3]. However, complexes of mono(tertiary)phosphines (PR_3), $[M(N_2)_2(PR_3)_4]$, give uncharacterisable products upon reaction with alkyl halides and lose all of their nitrogen as N_2 [4].

We have also shown that molybdenum [5] and tungsten [6] hydrazido(2—) complexes $[MX(NNH_2)(dppe)_2]^+$ (X = Cl, Br, or I) condense with aldehydes or ketones in the presence of catalytic amounts of acid to form diazoalkane complexes, some of which had already been obtained from reactions involving *gem*-dibromides. In this paper, we describe how hydrazido(2—) complexes which contain mono(tertiary)phosphines react with ketones (R^1R^2CO) to form diazoalkane complexes $[WX_2(=N{-}N{=}CR^1R^2)(PR_3)_3]$ which are unattainable by the direct reaction of *gem*-dibromides with the bis(dinitrogen) complexes, $[W(N_2)_2(PR_3)_4]$.

* Dedicated to Professor Ernst Otto Fischer on the occasion of his 60th birthday on November 10, 1978.

Results and discussion

The complexes $[W(N_2)_2(PR_3)_4]$ react with hydrogen halides HX in appropriate solvents to yield hydrazido(2—) complexes $[WX_2(NNH_2)(PR_3)_3]$. In this way the following hydrazido(2—) complexes have been prepared [7]: $[WBr_2(NNH_2)(PMe_2Ph)_3]$ (I), $[WCl_2(NNH_2)(PMe_2Ph)_3]$ (II), and $[WI_2(NNH_2)(PMe_2Ph)_3]$ (III). Further protonation to yield hydrazido(1—) complexes has also been achieved and compounds such as $[WCl_3(NHNH_2)(PMePh_2)_2]$ (IV) have been isolated [7]. The acid catalysed reactions of all four complexes with ketones are described here.

The reaction of I, or of its derivative, $[WBr(NNH_2)(PMe_2Ph)_4]Br$, with ketones ($R^1R^2CO$) in the presence of traces of aqueous hydrogen bromide produces brown, crystalline diazoalkane complexes $[WBr_2(N_2CR^1R^2)(PMe_2Ph)_3]$ (V) in moderate yield. Complexes II and III yield analogous materials. These complexes are air-stable in the solid state (Table 1), and are characterised by a strong band in their IR spectra at ca. 1520—1590 cm^{-1} assignable to ν(C=N). A similar band is found [3] in the IR spectra of the diazoalkane complexes, $[WBr(=N—N=CR^1R^2)(dppe)_2]^+$. The ^1H and ^{13}C NMR spectra taken in air-saturated solvents show the presence of paramagnetic species, but when the compounds are made up in dry solvents with exclusion of air the spectra (Table 2) are characteristic of diamagnetic complexes, having a *meridional* configuration of phosphines. The substituents R^1 and R^2 are in inequivalent positions (see Fig. 1) *.

Thus the complex $[WI_2(=N—N=CMe_2)(PMe_2Ph)_3]$ in CD_2Cl_2 gives rise to two singlets (τ 8.86, 8.73, intensity of each = 3) assignable to inequivalent C—Me of the diazoalkane. The phosphine methyls give rise to resonances at τ 8.29 (doublet, intensity 6), 8.19 (triplet, intensity 6) and 7.81 (triplet, intensity 6) typical of virtually coupled *meridional* phosphines in a complex lacking a plane of symmetry containing the phosphines. The inequivalence of the diazoalkane substituents has also been demonstrated by X-ray structure analysis of $[WBr(=N—N=CMe_2)(dppe)_2]Br$ [6].

The ^{13}C NMR spectra of the complexes V have resonances at very low field (ca. 165—180 ppm, int. TMS) which are assignable to the unique diazoalkane carbon, CR^1R^2 (cf. $[WBr(=N—N=CR^1R^2)(dppe)_2]^+$) [3]. Thus $[WBr_2(N_2CMe_2)$-

(continued on p. 170)

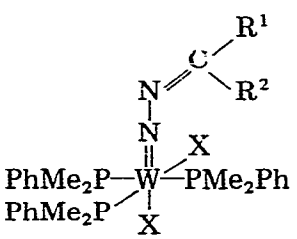

Fig. 1.

* In all the formulae in this paper the nitrogen ligands have been given formal valence bond structures but they are highly conjugated to the metal, e.g. see refs. 4 and 8.

TABLE 1

NEW COMPLEXES CONTAINING DIAZOALKANE AND HYDRAZIDO(1—) LIGANDS

Compound	Colour	Yield (%)	M.p. (dec.) (°C)	Analysis found (calcd.) (%)			
				C	H	N	Halogen
$[WCl_2(N_2CMe_2)(PMe_2Ph)_3]$	Brown	65	143—145	43.5 (43.9)	4.94 (5.32)	3.79 (3.78)	
$[WBr_2(N_2CMe_2)(PMe_2Ph)_3]$ [a]	Brown	65	142—144	38.9 (39.2)	5.03 (4.75)	3.37 (3.38)	19.5 (19.3)
$[WI_2(N_2CMe_2)(PMe_2Ph)_3]$	Dark brown	68	172—174	35.4 (35.2)	4.83 (4.27)	3.14 (3.04)	
$[WBr_2(N_2CMeEt)(PMe_2Ph)_3]$	Brown	36		40.0 (39.9)	4.94 (4.91)	3.39 (3.33)	
$[WBr_2(N_2CMePh)(PMe_2Ph)_3]$ [b]	Brown	72	150—154	43.2 (43.2)	4.83 (4.64)	3.11 (3.15)	
$[WBr_2\{N_2C(CH_2)_5\}(PMe_2Ph)_3]$	Brown	66	144—146	41.7 (41.5)	4.94 (4.99)	3.24 (3.23)	18.6 (18.4)
$[WBr_2\{N_2CMe(CH_2COMe)\}(PMe_2Ph)_3]$	Brown	20	110—118	39.8 (40.2)	4.66 (4.75)	3.05 (3.22)	18.5 (18.4)
$[WBr_2\{N_2CMe(CH_2CH_2COMe)\}(PMe_2Ph)_3]$	Brown	27	114—115	40.9 (40.8)	4.73 (4.90)	3.26 (3.17)	
$[WBr(N_2CMe_2)(8\text{-hq})(PMe_2Ph)_3]Br$ [c]	Purple	60	137—142	48.0 (48.5)	5.07 (5.08)	4.65 (4.71)	
$[WCl_3(NHNCMe_2)(PMePh_2)_2]$	Brown	12		45.6 (45.7)	4.68 (4.37)	3.34 (3.68)	
$[WBr_3(NHNCMe_2)(PMe_2Ph)_3]$ (VI)	Grey	77	135—137	35.6 (35.7)	4.71 (4.43)	3.09 (3.08)	26.7 (26.4)
$[WCl_3\{NHNCMe(CH_2COMe)\}(PMePh_2)_2]$	Yellow	22		46.2 (46.3)	4.60 (4.39)	3.51 (3.49)	
$[WCl_3(NHNCMe_2)(PMe_2Ph)_3] \cdot HCl$ (IX)	Yellow	40		39.8 (39.9)	4.90 (5.01)	3.34 (3.45)	
$[WBr_3(NHNCMe_2)(PMe_2Ph)_3] \cdot HBr$ (VII)	Yellow	40		33.1 (32.8)	4.64 (4.17)	2.95 (2.83)	

[a] Analogue prepared from $(CD_3)_2CO$ in 60% yield. [b] Mol. wt. (osmometric, 1,2-dichloroethane) 845 (calcd. 890). [c] Analogue prepared from $(CD_3)_2CO$ in 65% yield; molar conductivity 93 ohm^{-1} cm^2 mol^{-1} ($MeNO_2$).

TABLE 2

INFRARED AND NMR SPECTRA OF NEW COMPLEXES

	ν(C=N) (cm^{-1})	^{1}H NMR (alkyl region) τ [a]		^{13}C NMR (ppm, downfield from TMS)
$[WCl_2(N_2CMe_2)(PMe_2Ph)_3]$	1582			168.67 (N=C); 24.75, 22.33 $[C(\underline{C}H_3)_2]$
$[WBr_2(N_2CMe_2)(PMe_2Ph)_3]$	1582	8.35t(6) 8.08t(6) 8.40d(6) 8.59(3) 8.75(3)	*trans* PCH_3 PCH_3 (*cis*) br, m, CMe_2	168.04 (N=C); 24.95, 23.30 $[C(\underline{C}H_3)_2]$
$[WBr_2\{N_2C(CD_3)_2\}(PMe_2Ph)_3]$	1570	8.02t(6) 8.29t(6) 8.38d(6)	*trans* PCH_3 PCH_3 (*cis*)	
$[WI_2(N_2CMe_2)(PMe_2Ph)_3]$	1583	7.81t(6) 8.19t(6) 8.29d(6) 8.73s(3) 8.86s(3)	*trans* PCH_3 PCH_3 (*cis*) $NC(CH_3)_2$	162.97 (N=C); 20.36, 24.63 $[C(\underline{C}H_3)_2]$
$[WBr_2(N_2CMeEt)(PMe_2Ph)_3]$	1572	8.06t(6) 8.32t(6) 8.40d(6) 8.56m, 9.10m(8)	*trans* PCH_3 PCH_3 (*cis*) $NC(CH_3)(CH_2CH_3)$	
$[WBr_2(N_2CMePh)(PMe_2Ph)_3]$	1537, 1520(sh)	8.03t(6) 8.22t(6) 8.27d(6) 8.40s(3)	*trans* PCH_3 PCH_3 (*cis*) NCH_3	177.59 (N=C); 19.35 $[C(\underline{C}H_3)]$
$[WBr_2\{N_2C(CH_2)_5\}(PMe_2Ph)_3]$	1569, 1562(sh)	8.08t(6) 8.30t(6) 8.34d(6) 7.76m 8.40m(10)	*trans* PCH_3 PCH_3 (*cis*) $NC(CH_2)_5$	
$[WBr_2\{N_2CMe(CH_2COMe)\}(PMe_2Ph)_3]$	1572[ν(C=O) 1715]	7.9—9.0m(21) 8.00s(1.5) 7.87s(1.5) 6.86s(1) 5.13s(0.5)	PCH_3 and $NC(CH_3)$ $C(OH)C\underline{H}_3$ $COC\underline{H}_3$ $C\underline{H}_2COCH_3$ $=C \cdot C\underline{H}=$	

$[WBr_2\{N_2CMe(CH_2CH_2COMe)\}(PMe_2Ph)_3]$	1577[ν(C=O) 1723]		
$[W(N_2CMe_2)(8\text{-hq})(PMe_2Ph)_3]Br$	1584	8.73t(6) 8.78t(6)	*trans* PCH_3
		8.08d(6)	PCH_3 (*cis*)
		8.01s(3) 8.07s(3)	$NC(CH_3)_2$
$[W\{N_2C(CD_3)_2\}(8\text{-hq})(PMe_2Ph)_3]Br$	1563	8.73t(6) 8.78t(6)	*trans* PCH_3
		8.08d(6)	PCH_3 (*cis*)
$[WCl_3(NHNCMe_2)(PMePh_2)_2]$	1573, 1562(sh)	7.44m(6)	PCH_3
		8.40s(3) 8.42s(3)	$NC(CH_3)_2$
		−3.85t(1)	N—H
$[WCl_3\{NHNCMe(CH_2COMe)\}(PMePh_2)_2]$	1573, 1563(sh)	7.50m(6)	PCH_3
	[ν(C=O) 1719]	8.39s, 8.49s(3)	$NC(CH_3)$
		7.82s, 8.05s(3)	$-C(O)CH_3 + =C(OH)CH_3$
		6.7s(1)	$-COCH_2CO-$
		5.2s(0.5)	—CH=C
		−2.2s(0.5)	C=C(OH)
		−3.24t, −3.74t	W—N(H)
		−3.86t(1)	
$[WCl_3(NHNCMe_2)(PMe_2Ph)_3] \cdot HCl$	[ν(NH) 2980,	7.8—8.2m(~19)	PCH_3 and $NC(CH_3)_2$
	2800; further	8.98s(~5)	PCH_3 (free phosphine)
	characteristic	−2.04s(1)	β-NH
	band at 1395]	−2.20t	α-NH
		(1, $\lvert^3J$(P—H)$\rvert$ 90 Hz)	
$[WBr_3(NHNCMe_2)(PMe_2Ph)_3] \cdot HBr$	[ν(NH) 2990,	7.4—8.4m(~20)	PCH_3 and $NC(CH_3)_2$
	2790; further	8.92d(~4)	PCH_3 (free phosphine)
	characteristic	−0.65t	α-NH
	band at 1395]	(1, $\lvert^3J$(P—H)$\rvert$ 94 Hz)	
		−0.76s(1)	β-NH
$[WBr_3(NHNCMe_2)(PMe_2Ph)_3]$	1610[ν(NH) 2400]	8.85s(3) 8.33s(3)	$NC(CH_3)_2$
		8.45t(6) 8.03t(6)	*trans* PCH_3
		8.17d(6)	PCH_3 (*cis*)

[a] s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.

$(PMe_2Ph)_3$] has a resonance in CD_2Cl_2 at 168.04 ppm downfield from TMS which we assign to the unique carbon of diazopropane, and also singlets at 23.30 and 24.95 ppm which arise from the inequivalent methyls of the diazopropane.

We have also obtained a 2-diazopropane complex from [W(=N—NH_2)(8-hq)-$(PMe_2Ph)_3$]Br [7] (8-hq = 8-hydroxyquinolinate ion) and acetone. This product, [W(=N—N=CMe_2)(8-hq)$(PMe_2Ph)_3$]Br, is analogous to the complexes already described.

Removal of the new organonitrogen ligands from the metal as amines or hydrazines

The complexes [WBr_2(=N—NH_2)$(PMe_2Ph)_3$] react readily with acids to give good yields of ammonia, together with some hydrazine [7], also the diazoalkane complex [WBr(=N—N=CH_2)$(dppe)_2$]$^+$ reacts with nucleophiles, e.g. $LiAlH_4$ or LiMe to give organodiazenido complexes [WBr(—N=N—CH_2R)$(dppe)_2$] (R = H or Me) [3]. The reactions of the above reagents with the new organodiazoalkane complexes were therefore investigated in attempts to remove the diazoalkane ligand as an amine or substituted hydrazine.

The reaction of [WBr_2(=N—N=CMe_2)$(PMe_2Ph)_3$] with LiMe in Et_2O produces a red solution from which only a red oil was isolated. On the other hand, $LiAlH_4$ in excess produces a green solution, which, in a matter of hours, slowly turns yellow, and from which i-$PrNH_2$ was isolated in over 90% yield. The second nitrogen atom apparently yields ammonia, of which about 60% was recovered. Similarly, [WBr_2{=N—N=$C(CH_2)_5$}$(PMe_2Ph)_3$] produces $(CH_2)_5CHNH_2$ (90%) and NH_3 (65%) (Table 3). The tungsten-containing products have not yet all been characterised, but they include [$WH_6(PMe_2Ph)_3$] [9].

The diazoalkane complexes V also react with acids HX (X = Cl, Br, or I) in stepwise fashion, the precise mode of reaction depending upon X and the solvent. Thus [WBr_2(=N—N=CMe_2)$(PMe_2Ph)_3$] reacts with 1 mol of HBr in dichloromethane solution to yield, when immediately precipitated by ether, a greyish-green material, tentatively formulated as [WBr_3(=NH—N=CMe_2)$(PMe_2Ph)_3$] (VI), but it slowly disproportionates to produce more highly protonated material and [WBr_2(=N—N=CMe_2)$(PMe_2Ph)_3$] in CH_2Cl_2 solution. The ^1H NMR spectrum of VI confirms the presence of three *meridional* phosphines, but the N—H proton resonance was not observed. In the IR spectrum of VI, ν(C=N) is

TABLE 3

YIELDS OF AMMONIA, HYDRAZINE AND AMINES

Complex	Reaction	Products (yields %) [a]	
[$WBr_2(N_2CMe_2)(PMe_2Ph)_3$]	$LiAlH_4$ reduction	i-$PrNH_2$	(93, 95)
		NH_3	(60, 55)
[WBr_2{$N_2C(CH_2)_5$}$(PMe_2Ph)_3$]	$LiAlH_4$ reduction	$C_6H_{11}NH_2$	(91, 88)
		NH_3	(65, 65)
[$WBr_2(N_2CMe_2)(PMe_2Ph)_3$]	HBr	N_2H_4	(64, 57)
		NH_3	Nil
		i-$PrNH_2$	Nil
		Me_2C=N—N=CMe_2	(25, 30)

[a] Two independent determinations.

found at 1610 cm^{-1} considerably shifted compared to the diazoalkane parent (1582 cm^{-1}, Table 2), and a broad band at 2400 cm^{-1} is probably ν(NH) in —NH—N=C. Recently it has been observed that VI can also be generated from $[WBr_3(NHNH_2)(PMe_2Ph)_3]$ and acetone [10]. The iodo analogue of VI is less labile, but the chloro analogue was too labile to be isolated pure.

Treatment of VI with a further mole of HBr yields a pale yellow non-ionic adduct $[WBr_3(—NH—N=CMe_2)(PMe_2Ph)_3] \cdot HBr$ (VII) of unknown structure. Its IR spectrum shows a band at 1395 cm^{-1} and bands at 2790 and 2990 cm^{-1} assignable to ν(NH). Its ^1H NMR spectrum can be interpreted in terms of a slow equilibrium dissociation to yield PMe_2Ph and $[WBr_3(—NH—NH—CMe_2Br)(PMe_2Ph)_2]$ (VIII). Thus resonances at τ —0.65 (triplet, intensity 1, $|^3J(P—H)|$ 94 Hz, indicating *trans* phosphines) and τ —0.76 (singlet, intensity 1) are assigned to W—N<u>H</u>—NH(α) and W—NH—N<u>H</u>(β) protons, respectively. The β-N—H exchanges rapidly on addition of D_2O to a solution in CD_2Cl_2, whereas the α-N—H if it exchanges does so very slowly. Slow exchange is characteristic of such α-protons [11]. A reasonable formulation of the structure of VIII is that given above, but the position of the bromine from the HBr is not proven.

Addition of 10 *M* eq. of HBr to $[WBr_2(=N—N=CMe_2)(PMe_2Ph)_3]$ gives after 18 h a red solution from which $[WBr_4(PMe_2Ph)_2]$ was isolated in 65% yield. Presumably complexes VI—VIII are intermediates. Also $N_2H_4 \cdot 2\,HBr$ was isolated, and the GLC analysis of the red solution indicated the presence of acetone azine, $Me_2C=N—N=CMe_2$ (25—30% yield). No ammonia or 2,2-dibromopropane was detected. Probably acetone hydrazone which is known to rearrange to hydrazine and acetone azine [12], is initially formed. The reaction does not involve the intermediate formation of the complex $[WBr_2(=N—NH_2)(PMe_2Ph)_3]$ because, on treatment with 10 *M* eq. of HBr in dichloromethane, that yields ammonia (0.74 mol) and hydrazine (0.23 mol) [7]. The likely sequence leading to hydrazine and acetone azine is as follows, but the formation of the C—Br bond is not yet proven.

$$[WBr_2(=N—N=CMe_2)(PMe_2Ph)_3] \xrightarrow{+HBr} [WBr_3(—NH—N=CMe_2)(PMe_2Ph)_3]$$

$$\xrightarrow{+HBr} [WBr_3(—NH—NHCMe_2Br)(PMe_2Ph)_3] \xrightarrow{-PMe_2Ph} [WBr_3(—NH—NHCMe_2Br)(PMe_2Ph)_2] \xrightarrow{+HBr} [WBr_4(PMe_2Ph)_2] + NH_2NHCMe_2Br \xrightarrow{-HBr} NH_2N=CMe_2$$

$$\rightarrow N_2H_4 + Me_2C=N—N=CMe_2$$

The complex $[WCl_2(=N—N=CMe_2)(PMe_2Ph)_3]$ is not changed by treatment with HCl (10 *M* eq.) in dichloromethane during 18 h at room temperature, except for the formation of small amounts of ammonia (0.05 mol) and hydrazine (0.07 mol). However with aqueous hydrochloric acid in THF solution, it yields what appears to be $[WCl_3(—NH—N=CMe_2Cl)(PMe_2Ph)_3] \cdot HCl$ (IX) analogous to VII. The ^1H NMR spectrum in CD_2Cl_2 solution shows a triplet, intensity 1, at τ —2.20 ($|^3J(P—H)|$ 90 Hz), suggestive of a W—N<u>H</u>-proton split by two phosphines, and a singlet at τ —2.04 assignable to the W—NH—N<u>H</u> proton. This is interpreted in terms of a dissociation (ca. 80%) into $[WCl_3(—NH—NHCMe_2Cl)(PMe_2Ph)_2]$ and PMe_2Ph. The latter can be identified by a doublet

resonance at τ 8.98, intensity 5 (intensity 6 would indicate complete dissociation).

Reactions of hydrazido(2—) complexes with diketones

The complex $[WBr_2(=N—NH_2)(PMe_2Ph)_3]$ also reacts with 2,4-pentanedione or 2,5-hexanedione, but only one carbonyl group of the diketone condenses, and we have no evidence of double condensations to produce a diketone residue bridging two tungsten moieties or the formation of heterocyclic ligands. The IR spectrum of $[WBr_2(=N—N=CMeCH_2COMe)(PMe_2Ph)_3]$ has a band at 1572 cm^{-1} which we assign to $\nu(C=N)$ and another at 1715 cm^{-1} which we assign to an uncoordinated $\nu(C=O)$. There is a further band at 1624 cm^{-1} which may be $\nu(C=C)$, but is more likely to be an OH bending vibration associated with an enol form of the ligand. This inference of keto-enol isomerism is confirmed by the ^1H NMR spectrum of the complex, which is best interpreted in terms of an equilibrium between roughly equal amounts of keto and enol forms (see Table 2).

$$=N—N=\overset{\overset{Me}{|}}{C}—CH_2COMe \rightleftharpoons =N—N=\overset{\overset{Me}{|}}{C}—CH=C(OH)Me$$

The hydrazido(1—) complex $[WCl_3(—NH—NH_2)(PMePh_2)_2]$ [7] also condenses with ketones such as acetone to yield alkylidenehydrazido(1—) complexes $[WCl_3(—NH—N=CR^1R^2)(PMePh_2)_2]$ (X). The IR spectrum of X, $R^1 = R^2 = Me$, shows a band at 1573 cm^{-1} assignable to $\nu(C=N)$. The ^1H NMR spectrum shows that the two methyl groups (singlets at τ 8.42 and 8.40) are not equivalent. There is also a triplet at τ —3.85 ($|^3J(P—H)|$ 90 Hz) which we assign to the α-proton. In the parent compound this triplet occurs at τ —2.10, $|^3J(P—H)|$ 92 Hz [7]. This proton does not exchange with protons in aqueous CD_2Cl_2, and the pyridine-catalysed exchange, if it occurs, is very slow.

The corresponding derivative from 2,4-pentanedione, $[WCl_3(NHNCMeCH_2COMe)(PMePh_2)_2]$, was prepared analogously. Its ^1H NMR spectrum is very complex and may be interpreted as arising from a mixture of keto and enol forms in approximately equal proportions. The olefinic proton in the enol form gives

$$WNH—N=\overset{\overset{Me}{|}}{C}CH_2COMe \rightleftharpoons WNH—N=\overset{\overset{Me}{|}}{C}CHC(OH)Me$$

(a) (b)

rise to a singlet resonance at τ 5.2, whereas the methylene protons of the keto tautomer produce a singlet at τ 6.7. The terminal methyl groups of the two tautomers produce two singlets (total intensity ca. 3 protons) at τ 8.05 and 7.82. The remaining methyl groups ($=N_2=CMe—$) produce two singlets, total intensity ca. 3, at τ 8.49 and 8.39 and the enolic —OH appears as a broad signal (0.5 protons) at τ —2.2.

The α-NH protons, in contrast to the OH, do not exchange with D_2O. The NH protons give rise to three triplets (total intensity 1) each with $|^3J(P—H)|$ 90 Hz. This suggests that the compound exists in solution as a mixture of three isomers each with *trans* phosphines.

Conclusion

In this work we have shown that hydrazido(2—)- and hydrazido(1—)-complexes undergo Schiff-type condensation with ketones in the presence of acid. Diketones also condense but do not form heterocycles, probably due to steric hindrance by the other ligands. The condensation products can be reduced to amines with an excess of lithium aluminium hydride, or can be protonated stepwise to form, eventually, hydrazine and the keto-azine.

Experimental

The complexes $[WX_2(NNH_2)(PMe_2Ph)_3]$ (X = Cl, Br, or I), $[W(NNH_2)(8\text{-hq})(PMe_2Ph)_3]Br$, and $[WCl_3(NHNH_2)(PMePh_2)_2]$ were synthesised by literature methods [7]. All manipulations were carried out under dry dinitrogen using standard Schlenk-tube techniques. The following spectrometers were used: Perkin—Elmer 457 (KBr discs) (IR), JEOL PS-100 (^{1}H NMR) and PFT-100 (^{13}C NMR) (generally CD_2Cl_2 solution, TMS as internal standard). Molecular weights were determined in solution in 1,2-dichloroethane using a Perkin—Elmer—Hitachi 115 vapor pressure osmometer. Melting points were measured in air. Analyses were by Mr. A.G. Olney, University of Sussex.

Dibromo(2-diazopropane)tris(dimethylphenylphosphine)tungsten. To a suspension of $[WBr_2(NNH_2)(PMe_2Ph)_3]$ (0.51 g) in acetone (0.70 cm^3) and dichloromethane (20 cm^3) was added one drop of concentrated (ca. 49%) hydrobromic acid. After stirring for about ten minutes a dark brown homogeneous solution was produced. After a further 7 h the volume was reduced at 10^{-3} mmHg to ca. 7 cm^3 and n-hexane (15 cm^3) added. A small amount of solid was filtered off and the dark brown filtrate slowly concentrated at 10^{-3} mmHg to yield brown crystals (0.35 g, 65%) which were filtered off, washed with pentane, and dried in vacuo.

In similar fashion were prepared dibromo(2-diazobutane)tris(dimethylphenylphosphine)tungsten, dichloro(2-diazopropane)tris(dimethylphenylphosphine)tungsten, (2-diazopropane)tris(dimethylphenylphosphine)diodotungsten, dibromotris(dimethylphenylphosphine)(1-phenyl-1-diazoethane)tungsten, and dibromo(diazocyclohexane)tris(dimethylphenylphosphine)tungsten, using the appropriate ketone. Products could not be obtained from benzophenone, acetaldehyde, or benzaldehyde.

Dibromo(2-diazopentan-4-one)tris(dimethylphenylphosphine)tungsten. Acetylacetone (0.50 cm^3) was added to $[WBr_2(NNH_2)(PMe_2Ph)_3]$ (0.25 g) suspended in dichloromethane (10 cm^3) in the presence of a trace of concentrated hydrobromic acid. After ca. 10 min the system became homogeneous, and the dark brown solution was then stirred for 5 h, when a small amount of precipitate was filtered off. The brown filtrate was taken to dryness at 10^{-3} mmHg and the residue extracted with hexane (20 cm^3). The extract was reduced to half-volume at 10^{-3} mmHg and left to stand at 0°C for 1 day. The pale brown solid which had deposited, was filtered off, washed with cold pentane and dried in vacuo (0.056 g, 20%).

Dibromo(2-diazohexan-5-one)tris(dimethylphenylphosphine)tungsten. To a

suspension of $[WBr_2(NNH_2)(PMe_2Ph)_3]$ (0.25 g) in acetonylacetone (0.5 cm^3) and dichloromethane (10 cm^3) was added one drop of concentrated hydrobromic acid. After 10 min stirring the mixture had become homogeneous, and it was then stirred for a further 5 h. A small amount of blue precipitate was removed by filtration and the filtrate taken to dryness at 10^{-3} mmHg. The brown oily residue was dissolved in diethyl ether (3 cm^3) and hexane (10 cm^3) added. Upon allowing to stand at 0° C, brown crystals separated. These were filtered off, washed with pentane, and dried in vacuo (0.075 g, 27%).

(2-Diazopropane)tris(dimethylphenylphosphine)(8-hydroxyquinolinato)-tungsten bromide. Acetone (0.90 cm^3) and one drop of concentrated hydrobromic acid were added to a purple solution of $[W(NNH_2)(8\text{-hq})(PMe_2Ph)_3]Br$ (0.55 g) in dichloromethane (10 cm^3). After stirring the solution for 24 h, it was reduced in volume to ca. 10 cm^{-3} at 10^{-3} mmHg and diethyl ether (40 cm^3) was slowly added. After 24 h purple crystals were filtered off, washed with diethyl ether and dried in vacuo (0.35 g, 60%).

Trichlorobis(methyldiphenylphosphine){N-(2-propylidene)hydrazido(1—)-N'} tungsten. Acetone (0.3 cm^3) and one drop of concentrated hydrochloric acid were added to a solution of $[WCl_3(NHNH_2)(PMePh_2)_2]$ (0.24 g) in dichloromethane (20 cm^3). After stirring for 20 h, the reddish brown solution was separated from a small amount of precipitate, and the filtrate taken to dryness at 10^{-3} mmHg. The residue was dissolved in THF (5 cm^3), diethyl ether (2 cm^3) added, and the mixture kept at 0° C. The brown precipitate was filtered off, washed with diethyl ether, and dried in vacuo (0.030 g, 12%). Addition of more diethyl ether (10 cm^3) to the filtrate produced a further amount of brown solid which could not be properly characterised.

Trichlorobis(methyldiphenylphosphine){N-(2-pentyliden-4-one)hydrazido-(1—)-N'}tungsten. Acetylacetone (0.20 cm^3) and one drop of concentrated hydrochloric acid were added to a solution of $[WCl_3(NHNH_2)(PMePh_2)_2]$ (0.18 g) in dichloromethane (20 cm^3). After stirring for 20 h, the solution was filtered and the brown filtrate taken to dryness at 10^{-3} mmHg. The residue was dissolved in THF (10 cm^3) and diethyl ether (10 cm^3) slowly added. Upon standing at 0° C, a yellow precipitate formed, which was filtered off, washed with diethyl ether, and dried in vacuo (0.045 g, 22%).

Tribromo-{N-(2-propylidene)hydrazido(1—)-N'}tris(dimethylphenylphosphine)tungsten. Hydrogen bromide (0.70 mmol) was condensed at —196° C onto a solution of $[WBr_2(NNCMe_2)(PMe_2Ph)_3]$ (0.58 g, 0.70 mmol) in dichloromethane (40 cm^3). On warming to room temperature a blue-green solution was obtained. After stirring for 15 min diethyl ether (100 cm^3) was added and the product precipitated as lustrous grey flakes which were filtered off, washed with diethyl ether (10 cm^3) and dried in vacuo. Yield 0.49 g (77%).

Tribromo-{N-(2-propylidene)hydrazido(1—)-N'}tris(dimethylphenylphosphine)tungsten-hydrogen bromide (1/1). Hydrogen bromide (0.54 mmol) was condensed at —196° C on to a solution of $[WBr_3(N(H)N{=}CMe_2)(PMe_2Ph)_3]$ (0.49 g, 0.54 mmol) in dichloromethane (40 cm^3) and the mixture was stirred for 18 h at room temperature. The brown-red solution was then concentrated to ca. 10 cm^3 and diethyl ether (50 cm^3) was added. On standing at 0° C, a yellow-green crystals of the product were deposited. These were filtered off, washed with ether and dried in vacuo. Yield 0.2 g (40%). The chloro analogue

was obtained by the reaction of concentrated hydrochloric acid (0.2 cm^3) with $[WCl_2(NNCMe_2)(PMe_2Ph)_3]$ (0.2 g). They were stirred in THF (40 cm^3) at room temperature for 72 h. Addition of hexane (40 cm^3) to the yellow-brown solution precipitated a yellow-green oil which was separated and crystallised as pale yellow needles from methanol, ether and hexane; these were filtered off, washed with hexane, and dried in vacuo. Yield 0.08 g (40%).

Reaction of $[WBr_2(N_2CMe_2)(PMe_2Ph)_3]$ or $[WBr_2\{N_2C(CH_2)_5\}(PMe_2Ph)_3]$ with $LiAlH_4$ and the formation of amines. The complex (0.15—0.20 g, weighed accurately) was placed in a Schlenk flask (capacity 50 cm^3) attached to a vacuum line and equipped with a solid delivery tube and a magnetic follower. Diethyl ether (20 cm^3) was condensed into the flask which was allowed to warm to room temperature. The delivery tube was then turned to allow $LiAlH_4$ (10-fold molar excess) to be added to the stirred suspension. A clear green solution was obtained, which, over 3 h, turned pale yellow. The mixture was cooled to liquid nitrogen temperature, methanol (5 cm^3) condensed in and the mixture stirred at room temperature for 10 min. Hydrogen bromide gas (20-fold molar excess) was then condensed in, and the mixture, warmed to room temperature, stirred for 0.5 h, taken to dryness, and the residue extracted with water (2 × 20 cm^3). The combined extract was made up to 50 cm^3 and aliquots used to determine ammonia (indophenol method) [13], hydrazine (*p*-dimethylaminobenzaldehyde method) [14], and amines (see below).

Reaction of $[WBr_2(N_2CMe_2)(PMe_2Ph)_3]$ and HBr to form hydrazine and acetone azine. The complex (0.15—0.20 g, weighed accurately) was placed in a Schlenk flask as described above. The solid was dissolved in CH_2Cl_2 (20 cm^3) and HBr gas (10-fold molar excess) condensed in at liquid nitrogen temperature. On warming a blue-green solution was obtained, and this turned green-brown, and after 18 h the solution was clear red. The solution was taken to dryness, the residue extracted with water (2 × 20 cm^3) and the combined extracts filtered and the filtrate made up to 50 cm^3 for determination of hydrazine and ammonia. The residue from extraction was recrystallised from CH_2Cl_2/C_6H_{14} to give dark-red crystals identified by elemental analysis and ^1H NMR spectroscopy.

Determination of amines and acetone azine. Amines were determined on a Pye 104 chromatograph fitted with a nitrogen-compound-selective thermionic detector and a 5 ft. column packed with 4% Carbowax 20M and 0.8% KOH on Carbopack B. Both internal and external standards were used. The amines were characterised by retention time, ^1H NMR spectroscopy, and colour tests (2,4-dinitrofluorobenzene). Acetone azine was characterised by its GLC retention time and by its mass spectrum (M^+ 112).

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