The Preparation and Reactions of Azidobis[1,2-bis(diphenylphosphino)ethane]nitridotungsten(IV)

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The complex $[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ and trimethylsilyl azide in toluene or tetrahydrofuran yield $[WN(N_3)(Ph_2PCH_2CH_2PPh_2)_2]$ in a reaction which probably involves free radicals. The nitrido-group in $[WN(N_3)(Ph_2PCH_2CH_2PPh_2)_2]$ is readily attacked by electrophiles to give imido-, alkylimido-, or thionitrosyl complexes.

TRIMETHYLSILYL AZIDE is a convenient reagent for preparing nitridomolybdenum compounds,[1] and the azidonitrido-complex $[MoN(N_3)(dppe)_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane] is the precursor of a series of imido- and nitrido-molybdenum complexes. We describe here the preparation of the analogue $[WN(N_3)(dppe)_2]$ and its reactions with electrophiles, and some preliminary observations on the mechanism of formation of these azidonitrido-complexes.

RESULTS AND DISCUSSION

The complex $[W(N_2)_2(dppe)_2]$ reacts with Me_3SiN_3, in a fashion similar to that of the molybdenum analogue, to yield $[WN(N_3)(dppe)_2]$ (1), but the reaction is considerably slower and irradiation is required. Using a variety of solvents [toluene, tetrahydrofuran (thf), or 1,4-dioxan at reflux] the yield of (1) never exceeded 40%.

The nitrido-group of (1) is, as in the molybdenum analogue, sufficiently basic to be protonated by aqueous perchloric acid or anhydrous hydrogen chloride in dichloromethane to give the azidoimido-complex salts $[W(NH)(N_3)(dppe)_2]ClO_4$ (2a) and $[W(NH)(N_3)(dppe)_2]Cl$ (2b), respectively. In contrast to the reaction between $[MoN(N_3)(dppe)_2]$ and a hydrohalic acid (HX) in methanol which results in the halidoimido-complex $[Mo(NH)X(dppe)_2]X$, treatment of the tungsten complex (1), under identical conditions, yields the azidoimido-complex (2). However, tungsten halidoimido-complexes can be prepared by treatment of (2b) with an excess of lithium methoxide in methanol, followed by acidification of the resulting solution with hydrohalic acid. This yields the halidoimido-complexes $[W(NH)X(dppe)_2]X$ (3a, X = F; 3b, X = Cl; 3c, X = Br; 3d, X = I). When the reaction with hydrofluoric acid was performed in a borosilicate glass flask the tetrafluoroborate salt was isolated.

This general synthesis employs the strong labilising in-

methane for 18 h. Treatment of (3c) with methyllithium in thf yields $[WN(Br)(dppe)_2]$ (5).

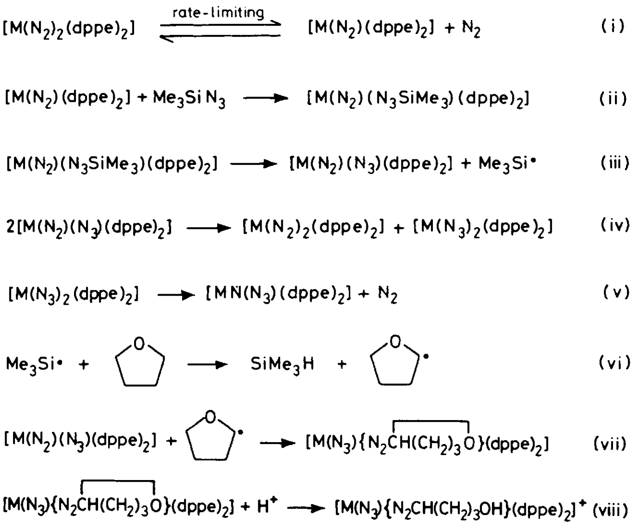
The halidoimido-complexes (3) cannot be protonated beyond the imido-stage, even with prolonged heating with aqueous acid in methanol under reflux. However, treatment of (3) with base in methanol gives ammonia in *ca.* 50% yield. Ammonia is only obtained after heating the solution under reflux for several hours, and then treating with acid, whereas the molybdenum analogues yield ammonia under ambient conditions. Prior to acidification, 1 mol equivalent of dppe (identified by i.r. and ^1H n.m.r. spectra, elemental analysis, and melting point) was isolated and a yellow solution formed. The ammonia is not evolved during the reflux, but only upon subsequent acid treatment of the reaction mixture. A yellow solid can be obtained from the yellow solution but this material never gave a comprehensible elemental analysis and the ^1H n.m.r. spectrum showed several peaks. It is almost certainly a mixture. These observations, together with the relatively low ammonia yields (*ca.* 50%), indicate that at the elevated temperatures necessary for this reaction, decomposition of the methoxo-complex (4) is also occurring.

Complex (1) reacts with EtI to yield the complex $[W(NEt)(N_3)(dppe)_2]I$ (6) which gives ethylamine upon destructive base distillation (gas-liquid chromatography, qualitative analysis only). 'Activated' aryl halides such as 1-fluoro-2,6-dinitrobenzene readily react with (1), but the products were not characterised.

Finally, complex (1) reacts with propylene sulphide to yield the thionitrosyl $[W(NS)(N_3)(dppe)_2]$ (7). Although this method has been used previously in molybdenum chemistry to synthesise thionitrosyls,[3] they were not dppe derivatives. Therefore the thionitrosyl complexes $[Mo(NS)(N_3)(dppe)_2]$ (8) and $[Mo(NS)Br(dppe)_2]$ (9) were prepared by the reaction of propylene sulphide with

There is strong evidence that free radicals are involved in the reaction between Me_3SiN_3 and $[M(N_2)_2(dppe)_2]$ (M = Mo or W). If $[W(N_2)_2(dppe)_2]$ and Me_3SiN_3 are allowed to react in thf, then $[W(N_3)\{N_2CH(CH_2)_3OH\}(dppe)_2]HSO_4$ (10) can be isolated in *ca.* 20% yield. This product must arise from radical attack upon thf.[4,5] The presence of co-ordinated azide also suggests that Me_3SiN_3 was attached to the metal.

It is proposed that the mechanism of the reaction between Me_3SiN_3 and $[M(N_2)_2(dppe)_2]$ is similar to that between alkyl halides and these same substrates. Thus the mechanism (Scheme) involves rate-limiting loss of N_2 (mediated by light for tungsten), followed by rapid co-ordination of Me_3SiN_3 and subsequent homolysis to yield $[M(N_2)(N_3)(dppe)_2]$. It seems unlikely that dinitrogen cleavage would occur in this complex to yield complex (1). We infer rather that, like the analogous $[MoCl(N_2)(dppe)_2]$,[4] $[M(N_2)(N_3)(dppe)_2]$ disproportionates to $[M(N_2)_2(dppe)_2]$ and $[M(N_3)_2(dppe)_2]$, the former reacting with more Me_3SiN_3 and the latter losing N_2 to



SCHEME

TABLE 1

Analysis and spectral properties of compounds

	Compound	Colour	M.p. (°C) with decomp.	Analysis [a] (%)			Spectral properties [b]
				C	H	N	
(1)	$[WN(N_3)(dppe)_2]$	Lemon-yellow	182—184	60.4 (60.2)	5.20 (4.65)	5.35 (5.40)	$\nu(N_3)$ 2 060vs; ν(WN) 980s. Mo analogue has bands at 2 025 and 972 [1]
(2a)	$[W(NH)(N_3)(dppe)_2]ClO_4$	Red-purple	207	54.6 (54.9)	4.55 (4.35)	4.75 (4.90)	ν(NH) 3 220w (br); $\nu(N_3)$ 2 095vs. No N*H* detectable in n.m.r. (CD_2Cl_2)
(2b)	$[W(NH)(N_3)(dppe)_2]Cl$	Red-purple	213	57.9 (58.1)	4.60 (4.55)	5.35 (5.20)	ν(NH) 3 220w (br); $\nu(N_3)$ 2 095vs
(3a)	$[W(NH)F(dppe)_2]BF_4$	Yellow	257—260	56.4 (56.6)	4.40 (4.45)	1.20 (1.25)	ν(NH) 3 300w (br). No N*H* detectable in n.m.r. ($CDCl_3$)
(3b)	$[W(NH)Cl(dppe)_2]Cl$	Orange	245	58.1 (58.4)	5.15 (4.60)	1.25 (1.30)	ν(NH) 3 350w (br). No N*H* detectable in n.m.r. ($CDCl_3$)
(3c)	$[W(NH)Br(dppe)_2]Br$	Red	252	53.7 (54.0)	4.35 (4.25)	1.35 (1.20) [c]	ν(NH) 3 400w (br). τ 0.1 (br, s, 1 H) assigned to N*H*, disappears upon addition of CD_3OD (in CD_2Cl_2)
(3d)	$[W(NH)I(dppe)_2]I\cdot0.5CH_2Cl_2$	Mauve	249	48.8 (48.2)	4.05 (3.85)	1.20 (1.05)	ν(NH) 3 420w (br). τ 0.8 (br, s, 1 H) assigned to N*H* ($CDCl_3$)
(4)	$[W(NH)(OMe)(dppe)_2]I$	Yellow	245	54.2 (54.0)	4.90 (4.25)	1.30 (1.30)	ν(NH) 3 380w (br). No N*H* detectable in n.m.r. τ 6.6 (s, 3 H) assigned to OC*H*$_3$ ($CDCl_3$)
(5)	$[WN(Br)(dppe)_2]$	Lemon-yellow	210	57.5 (58.1)	4.80 (4.45)	1.45 (1.30)	ν(WN) 980s (980 in Mo analogue)
(6)	$[W(NEt)(N_3)(dppe)_2]I$	Red-orange	159—162	54.6 (54.4)	4.90 (4.50)	4.30 (4.70)	New band at 1 270 compared to (1), $\nu(N_3)$ 2 100vs. τ 8.2 (m, 2 H, NC*H*$_2$), 10.0 [t, 3 H, C*H*$_3$, ^3J(H–H) = 7 Hz, CD_2Cl_2]
(7)	$[W(NS)(N_3)(dppe)_2]$	Red	144—146	58.1 (58.4)	5.10 (4.50)	5.20 (5.25) [d]	$\nu(N_3)$ 2 100vs; ν(NS) 1 080m
(8)	$[Mo(NS)(N_3)(dppe)_2]$	Orange	170—172	63.3 (63.8)	5.10 (4.95)	5.40 (5.70) [e]	$\nu(N_3)$ 2 065vs (br); ν(NS) 1 065s
(9)	$[Mo(NS)Br(dppe)_2]\cdot0.5CH_2Cl_2$	Orange	167—171	59.8 (59.4)	4.75 (4.65)	1.50 (1.30)	ν(NS) 1 065s
(10)	$[W(N_3)\{N_2CH(CH_2)_3OH\}(dppe)_2]HSO_4$	Grey	99—103	55.3 (55.1)	5.00 (4.70)	5.20 (5.75)	$\nu(N_2)$ 2 105s; ν(C=N) 1 572m (1 572 in Br analogue) τ 3.72 (t, 1 H, N=C*H*), 8.52 (m, 5 H, C*H*C*H*$_2$C*H*$_2$), 6.48 (t, 2 H, C*H*$_2$O) in CD_2Cl_2, *cf.* τ 4.38 (t), 8.96, 8.68 (m), 6.58 (t) in Br analogue

[a] Calculated values in parentheses. [b] I.r. given in cm^{-1} (vs = very strong, s = strong, m = medium, w = weak, br = broad); ^1H n.m.r. given in τ (t = triplet, m = multiplet, s = singlet). [c] Br = 13.1(13.8)%. [d] S = 3.25(3.30)%. [e] S = 3.25(3.25)%.

yield $[MN(N_3)(dppe)_2]$ (1). The diazobutanol complex (10) is formed in the competitive pathways (vi), (vii), and (viii).

However, the ultimate fate of the Me_3Si group is not clear. We were unable to detect Me_3Si radicals by e.s.r. spectroscopy, or any $SiMe_3H$ [generated in (iii)] by gas-liquid chromatography.

EXPERIMENTAL

All manipulations were carried out under dry dinitrogen using standard Schlenk-tube and vacuum-line techniques. Spectra were recorded on the following spectrometers: i.r., Perkin–Elmer 537 as KBr discs or Nujol mulls: ^{1}H n.m.r.,

solvent removed *in vacuo*, and the *product* crystallised as red needles from methanol–diethyl ether–hexane (0.40 g, 73%).

Bis[1,2-*bis*(*diphenylphosphino*)*ethane*]*imidoiodotungsten Iodide* (3d) *and Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*imidomethoxytungsten Iodide* (4).—Lithium methoxide (0.10 g, 2.6 mmol) was added to a solution of (2b) (0.50 g, 0.47 mmol) in methanol (30 cm^3). To the bright yellow solution was added concentrated hydriodic acid until the solution was strongly acidic. Yellow *needles* of (4) were deposited and removed by filtration (0.43 g, 78%). When the acidic solution of (4) was heated at reflux for 0.5 h, it became mauve. The solution was concentrated *in vacuo* to 10 cm^3 and the mauve *solid* removed by filtration. Recrystallisation from dichloromethane–diethyl ether afforded mauve *vacuo*, the residue suspended in MeOH (30 cm^3), and concentrated sulphuric acid (5 drops) added. Addition of hexane and diethyl ether to the brown solution afforded grey *crystals* after 1 week at 0 °C. These crystals were recrystallised from methanol–diethyl ether–hexane (yield *ca.* 20%).

Ammonia Analyses.—Typically, the yellow solution obtained after heating under reflux a solution of (4) with lithium methoxide was rendered acidic by the addition of concentrated hydrochloric acid and then the solvent was removed *in vacuo*. Dichloromethane was added to the resulting solid and the ammonium chloride extracted into a known volume of water. A sample (1 cm^3) of the aqueous layer was then subjected to the indophenol test.[7]

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