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## STUDIES ON THE REACTIVITY OF CARBYNE COMPLEXES OF TUNGSTEN AND MOLYBDENUM

*Solid carbyne complexes  $[W(CNRMe)(CNMe)(dppe)_2]^+$  ( $R=H, Me$ ) (also in solution for  $R=Me$ ) undergo protonation reactions at the isonitrile nitrogen yielding products formulated as bridging carbyne complexes  $[\{W(CNRMe)(dppe)_2\}_2(\mu-CNHMe)]^{4+}$  which undergo deprotonation and cleavage by their solvents. Deprotonation occurs in basic solvents yielding the parent species but in trifluoroacetic acid the carbyne ligand  $CNMe_2$  undergoes protonation at nitrogen leading to the formation of  $trans-[W(CNHMe)_2(CNHMe)(dppe)]^{3+}$ . Dealkylation of the carbyne ligand  $CNMe_2$  in  $trans-[Mo(CNMe)_2(CNMe)(dppe)]^+$  resulted from reaction with  $LiMe$  yielding the parent bisisonitrile complex.*

## 1 — INTRODUCTION

Isonitriles are susceptible to undergo electrophilic attack when ligating the strong  $\pi$ -donor  $d^6$  metal centre " $M(dppe)_2$ " ( $M=Mo, W$ ) and the formation of aminocarbyne complexes  $trans-[M(CNRMe)(CNMe)(dppe)_2]^+$  [(A),  $R=H$ ; (B),  $R=Me, Et$ ] has been reported from the primary step of N protonation ( $R=H$ ) [1] or from N alkylation ( $R=Me, Et$ ) [2] of  $trans-[M(CNMe)_2(dppe)_2]$ .

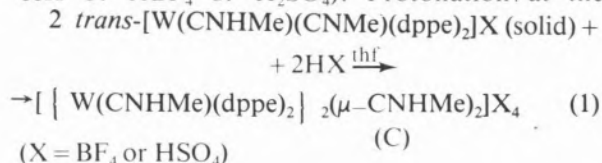
Complexes (A) and (B) are unstable in solution, an irreversible proton transfer from the carbyne to the metal occurring in the former, and a *trans*- to *cis*-isomerisation in the latter. Immediate and rapid acid addition to a solution of (A) yields the dicarbene complex [1, 3]  $trans-[M(CNHMe)_2(dppe)_2]^{2+}$  which is stable in solution and whose reactions have been reported in a previous paper [3]. The present study concerns the reactivity of the solid [(A),  $M=W$ ] and its dialkylaminocarbyne analogues (B).

## 2 — PROTONATION OF SOLID

$trans-[W(CNHMe)(CNMe)(dppe)_2]^+ (A)$

In an attempt to study the reactivity of a complex with a carbyne ligand, we have investigated the reactions of acid with (A) (which is unstable in solution as mentioned above) in the solid state.

Under these conditions, complexes (C) of a different type to those previously reported, [1-3] are formed from addition of acid to a suspension of (A) in thf (equation 1). They also precipitate from a concentrated thf solution of  $trans-[W(CNMe)_2(dppe)_2]$  upon dropwise acid addition (between 1.5 and a fourfold molar excess of  $HBf_4$  or  $H_2SO_4$ ). Protonation at the



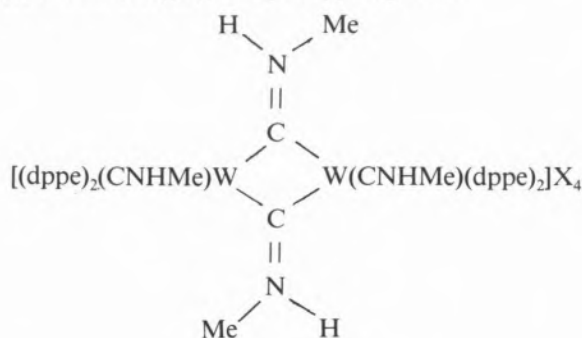
unreacted isocyanide appears to have occurred since there is no  $\nu (C \equiv N)$  stretching band in the product whereas a new band at *ca.*  $1620 \text{ cm}^{-1}$  has appeared. A strong absorption at  $3220 \text{ cm}^{-1}$  also appears (when using  $HBf_4$ ) which may be assigned to a N-H stretching band (Table I). Microanalyses agree with a diprotonated species. However, these species are

Table 1  
Dimeric bridging carbyne complexes  $\left\{ \left[ W(CNRM_e)(dppe)_2 \right]_2 (\mu - CNHMe)_2 \right\} X_4$

	R	X	Colour	$\Lambda_M^{(a)}$	M.p. <sup>(b)</sup> (°C)	yield (%)	Infrared <sup>(c)</sup>			Analysis <sup>(d)</sup>		
							$\nu(NH)$	$\nu(C=N)$	$\times$	C	H	N
(C1)	H	BF <sub>4</sub>	yellow	322	143-65	80	3220s	1620ms 1557s	1060vs	54.7(54.3)	4.8(4.7)	2.3(2.3)
(C2)	H	HSO <sub>4</sub> <sup>(e)</sup>	yellow	290	98dec	80	(f)	1624s 1565s	1245s 1169s 1153s 1065s	52.3(52.4)	4.6(4.7)	2.3(2.2)
(D1)	Me	BF <sub>4</sub>	yellow	320	108dec	98	3200ms,br	1624m 1563s	1060vs	54.3(54.7)	4.8(4.7)	2.2(2.2)
(D2)	Me	FSO <sub>3</sub> <sup>(g)</sup>	yellow	264	113dec	98	(h)	1624m 1566s	1295s } $\nu_{asym}(SO_3)^{(i)}$ 1268s } 1070ms } $\nu_{sym}(SO_3)$ 590sh } $\nu_{asym}(SO_3)^{(i)}$ 585m }	48.8(48.8)	4.3(4.1)	2.0(2.0)
(D3)	Et	BF <sub>4</sub> <sup>(i)</sup>	yellow	354	152dec	71	3210m,br	1618m 1558s	1065vs	50.0(52.4)	4.5(4.6)	2.1(2.1)

(a) Molar conductivity ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) in  $ca\ 10^{-3} \text{ M}$  nitrobenzene solution. Half of the reported values for monomeric species (from bridge split in solution). (b) In sealed evacuated tubes. (c) Nujol Mull. (d) Calculated values in parentheses. (e) Contains  $1/2 \text{ H}_2\text{SO}_4$ , hydrogen bonded. (f) Strong and very broad from  $ca. 3250 \text{ cm}^{-1}$  to lower wavenumbers until buried under Nujol [ $\nu(NH...O)$ ]. (g) Each monomeric unit contains one HFSO<sub>3</sub>, hydrogen bonded. (h) Very broad from  $ca. 3400 \text{ cm}^{-1}$  to lower wavenumbers [ $\nu(NH...O)$ ] until obscured by Nujol bands. (i) Splitting due to hydrogen bonding. (j) One CH<sub>2</sub>Cl<sub>2</sub> of crystallisation for each monomeric unit.

very poorly soluble in common organic solvents such as CH<sub>2</sub>Cl<sub>2</sub> and MeOH, in which all the carbyne and carbene complexes described [1, 3] previously are very soluble. Moreover, they are very unstable (*vide infra*) in the basic solvents in which they are soluble (e.g., pyridine, acetone, DMSO). This behaviour contrasts with the dicarbene complexes which can be prepared in solvents as basic as pyridine. These compounds (C) have a different formulation and a possible structure which is consistent with the available data (but which could only be unambiguously assigned by X-rays) is the dimer shown below with bridging carbyne type ligands:

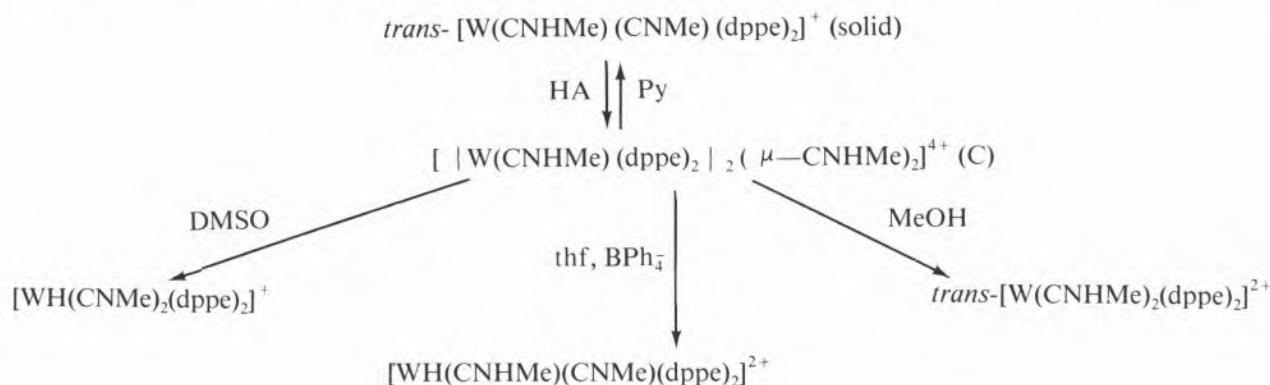


Such bridging moieties  $\mu - CNHR$ , also formed upon protonation at ligating isonitrile, are known to occur in other systems, namely  $[Cp_2Fe_2(CO)_2(\mu - CNHR)_2]^{2+}$  and  $[Cp_2Fe_2(CO)_2(\mu - CO)(\mu - CNHR)]^+$  (with R = Me, Et, CH<sub>2</sub> Ph), and the  $\nu(C=N)$  stretching bands which appears at  $ca. 1600 \text{ cm}^{-1}$  are comparable to those of our complexes (Table 1) [4].

The product from the H<sub>2</sub>SO<sub>4</sub> reaction shows a  $\nu(NH)$  i.r. band which is broader and shifted to a lower value than that of the analogous complex from the HBF<sub>4</sub> reaction and of the parent monocarbonyl complex *trans*-[W(CNHMe)(CNMe)(dppe)<sub>2</sub>](HSO<sub>4</sub>). Moreover, this parent species has three bands at 1242s, 1166s and 1065s  $\text{cm}^{-1}$  [assigned to  $\nu(SO)$  of uncoordinated HSO<sub>4</sub> ( $C_{3v}$  symmetry):  $\nu_{3a}$  ( $A_1$ ),  $\nu_{3b}$  ( $E$ ) and  $\nu_1$  ( $A_1$ ), respectively] [5], but the degeneracy of the mode giving the band at 1166  $\text{cm}^{-1}$  appears to be removed in the product since it is replaced by two bands at 1169 and 1153  $\text{cm}^{-1}$ , whereas the other two remain nearly unchanged at 1245 and 1065  $\text{cm}^{-1}$ . These facts may be explained by hydrogen bonding between N-H and HSO<sub>4</sub><sup>-</sup>. This is also in

agreement with microanalytical data which show the presence of an excess of 0.5 H<sub>2</sub>SO<sub>4</sub> per molecule. The dppe absorptions of the dimeric complexes also show some alterations relative to the parent monocarbene complex, *e.g.*, in the 800-900 cm<sup>-1</sup> region, in agreement with an alteration of the dppe conformation. The proposed dimeric species are deprotonated by pyridine leading to the parent monocarbene complex and by DMSO giving the hydride species. When the anion is exchanged for BPh<sub>4</sub> they go into solution (thf) giving the hydrido-carbyne complexes. In methanol the dicarbene complex, [W(CNHMe)<sub>2</sub>(dppe)<sub>2</sub>]<sup>2+</sup>, is formed. Hence solution studies on those species are precluded. These reactions are summarized in Scheme 1.

only soluble in basic solvents (pyridine, acetone, DMSO) where deprotonation occurs. This close similarity of properties with complexes (C) leads us to formulate these products as the analogous of (C) [ | W(CNRMe)(dppe)<sub>2</sub> |<sub>2</sub>(μ - CNHMe)<sub>2</sub>]X<sub>4</sub> (R = Me, Et) (D) (Table 1). In pyridine or in acetone solution the complexes are easily deprotonated by the basic solvent yielding the parent red complex *cis*-[W(CNRMe)(CNMe)(dppe)<sub>2</sub>]X. The same thing happens when the complexes go into thf solution upon anion substitution by BPh<sub>4</sub>. However, in trifluoroacetic acid (TFA) further protonation occurs and the <sup>1</sup>H n.m.r. spectrum of the product for (R = Me) is consistent with the formulation *trans*-[W(CNHMe)<sub>2</sub>(CNHMe)(dppe)<sub>2</sub>]<sup>3+</sup> (E) (Table



Scheme 1.

Preparation and reactivity of dimeric bridging alkylaminocarbyne complexes of W

### 3 — REACTIVITY OF DIALKYLAMINOCARBENE COMPLEXES [M(CNRMe)(CNMe)(dppe)<sub>2</sub>]<sup>+</sup> (B)

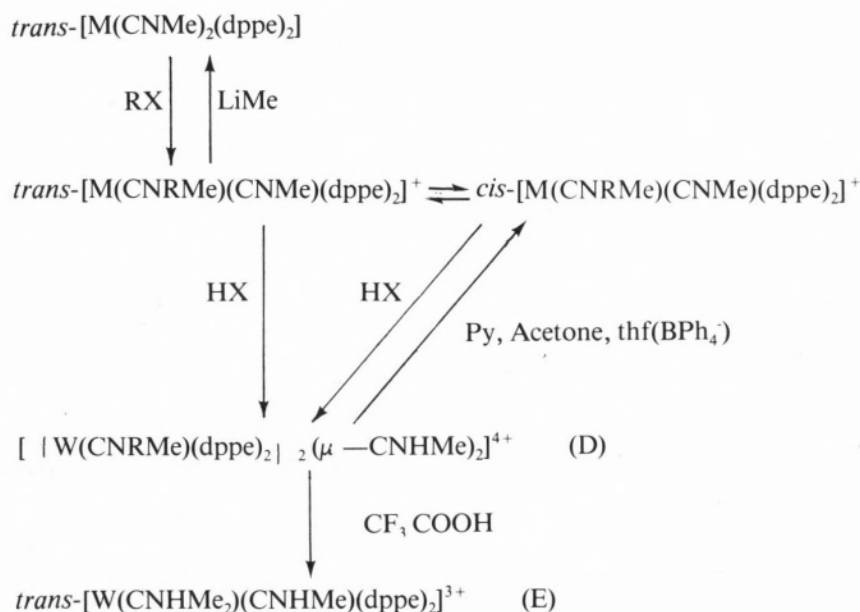
Addition of HBF<sub>4</sub> (or HFSO<sub>3</sub>) (7 equivalent acid excess) to a suspension of *trans*-[W(CNMe)<sub>2</sub>(CNMe)(dppe)<sub>2</sub>]FSO<sub>3</sub> in thf (or in C<sub>6</sub>H<sub>6</sub> respectively) or to a solution of *cis*-[W(CNEtMe)(CNMe)(dppe)<sub>2</sub>]BF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>, resulted in the suspension changing colour from green to yellow or in the precipitation of a yellow species, respectively. The i.r. spectra of the complexes formed show the disappearance of ν(C≡N) and the appearance of a new ν(C=N) at *ca.* 1620 cm<sup>-1</sup> and of a band at wave-numbers ≥ 3200 cm<sup>-1</sup> which may be assigned to ν(NH). Hence protonation at N of the MeNC appears to have occurred. However, in contrast to monomeric carbyne complexes, these products are

2). The *trans*- configuration has been assigned on the basis of the absence of the two triplets of the *ortho*-phenyl protons in the <sup>1</sup>H n.m.r. spectrum. Microanalytical and i.r. data for (E), isolated from TFA solution, indicate the inclusion of hydrogen-bonded acid. There appears to be a similar inclusion in complex (D2) of Table 1 because the degeneracy of the infrared E modes (1285<sub>vs</sub> and 585<sub>ms</sub>) of FSO<sub>3</sub><sup>-</sup> is removed by a decrease of its C<sub>3v</sub> symmetry leading to small splittings of these modes (27 cm<sup>-1</sup> and *ca.* 5 cm<sup>-1</sup>, respectively). This constitutes a minor alteration when compared to other complexes with well characterised coordinated FSO<sub>3</sub> [6].

The aforementioned reactions clearly show the nucleophilicity of the dialkylaminocarbyne complexes towards protonating agents. Their susceptibility to undergo nucleophilic attack was tested by treating a

suspension of *trans*-[Mo(CNMe)<sub>2</sub>(CNMe)(dppe)<sub>2</sub>] FSO<sub>3</sub> with LiMe in ether. The reaction resulted in dealkylation leading to the parent complex.

The abovementioned reactions are summarized in scheme 2.



Scheme 2  
Reactivity of dialkylaminocarbyne complexes  
of W and Mo

Table 2  
Collected data on  
trans-[W(CNHMe)<sub>2</sub>(CNHMe)(dppe)<sub>2</sub>](CF<sub>3</sub>COO)<sub>3</sub> (E)<sup>(a)</sup>

Colour	violet	<sup>1</sup> H n.m.r. (d)	τ	Integration	Assignment
Yield	87%		1.9-3.2m	40(40)	dppe aromatic
Λ <sub>M</sub>	218 <sup>(b)</sup>		4.1-4.5m, br <sup>(e)</sup>	2(2)	CNHMe <sub>2</sub> + CNHMe
I.r. (Nujol mull)	ν(NH) [ν(ND)] <sup>(c)</sup> = 3390m(2510), 3142wm(2320)		6.7-7.5m, br	12(12)	dppe methylene
	ν(C=N) = 1650s		7.18d <sup>(f),(g)</sup>		CNHMe
	CF <sub>3</sub> COO absorptions = 1793s, 1763s (COO), 1120-1160vs, br (CF <sub>3</sub> COO)		8.70d <sup>(g),(h)</sup>	6(6)	CNHMe <sub>2</sub>
Analyses	C, 50.3(50.8); H, 4.2(3.9); N, 1.8(1.8).				

(a) Contains 2CF<sub>3</sub>COOH, hydrogen bonded. (b) In ca. 10<sup>-3</sup> M nitrobenzene solution (Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>). (c) With a very broad and strong absorption from ca. 3300 cm<sup>-1</sup> to lower wavenumbers until obscured by Nujol [ν(N-H...O)] and/or [ν(OH...O)].

(d) TFA solution of complex (D). τ values relative to internal TMS, ±0.01. (e) Disappears upon D<sub>2</sub>O addition. (f) <sup>3</sup>J = 3.5 ± 0.5 Hz. (g) Collapses into a sharp singlet upon D<sub>2</sub>O addition. (h) <sup>3</sup>J = 5.0 ± 0.5 Hz.

#### 4 — FINAL REMARKS

Whereas different types of species (hydride, hydride-carbyne, dicarbene and possible bridging carbyne complexes) are derived by acid treatment of molybdenum and tungsten mixed isonitrile-amino-methylcarbyne (CNHMe) complexes, under the same conditions the more stable analogous dialkylaminocarbyne species  $[M(CNRMe)(CNMe)(dppe)_2]^+$  (R = alkyl) only reproduce the formation of the possible bridging carbyne complexes. Steric factors (opposing the alkyl migration from the carbyne ligand CNRMe to the metal) and a greater affinity of nitrogen for the proton than for the carbocation conceivably play a role in the difference between the observed behaviour. Nevertheless, the electron rich character of the  $CNMe_2$  carbyne ligand parallels that previously observed [3] for CNHMe and the carbyne group  $CNHMe_2$  is formed by protonic attack at nitrogen of the former.

#### 5 — EXPERIMENTAL

All the reactions were carried out under dinitrogen; thf, methanol and pyridine were dried and freshly distilled, under dinitrogen, from sodium benzophenone ketyl, magnesium methoxide and calcium hydride, respectively. The complexes *trans*- $[M(CNR)_2(dppe)_2]$  [7], (A) [1] and (B) [2] were prepared by published methods and the other reagents used as purchased. Infrared spectra were recorded on a Perkin Elmer 577 and n.m.r. spectra on a Jeol PS100 spectrometer. Conductivities were obtained by using a Portland Electronics P310 conductivity bridge and uncorrected melting points measured in a Electrothermal melting point apparatus.

##### 5.1 — PREPARATION OF POSSIBLE DIMERIC BRIDGING CARBYNE COMPLEXES (C)

e.g., *bis*( $\mu$ -methylaminocarbyne)-*bis*(methylaminocarbyne)tetrakis[1,2-bis(diphenylphosphino)ethane] ditungsten tetrakis(tetrafluoroborate)

Fluoroboric acid (0.602 g of a freshly prepared solution obtained by 1:11 dilution of  $Et_2OH^+BF_4^-$  in thf; 0.395 mmol acid) was added dropwise to a solu-

tion of *trans*- $[W(CNMe)_2(dppe)_2]$  (0.105g, 0.0988 mmol) in thf (10 cm<sup>3</sup>). The solution colour initially darkened probably due to the formation of the monocarbene complex *trans*- $[W(CNHMe)(CNMe)(dppe)_2]BF_4$  which may be isolated from the solution by a similar reaction with  $H_2SO_4$  (*vide infra*), but a yellow suspension began to appear, near the end of the addition, whose amount increased during a few minutes. After about 0.5h the suspension of the complex formulated as  $[|W(CNHMe)(dppe)_2|_2(\mu-CNHMe)_2](BF_4)_4$  was separated from the solution by filtration and was washed with thf, then dried (0.098g, 80% yield).

A similar product (with  $HSO_4^-$  instead of  $BF_4^-$ ) is obtained from thf solution in similar yield, by replacement of  $HBf_4$  by  $H_2SO_4$  | from two- to four-fold molar excess relative to *trans*- $[W(CNMe)_2(dppe)_2]$  using the above procedure.

However, during the initial dropwise acid addition, the green monocarbene *trans*- $[W(CNHMe)(CNMe)(dppe)_2]HSO_4$  precipitates out of the solution since it is less soluble than its  $BF_4$  analogue. The colour of this suspension changes to yellow during further addition of acid, giving the proposed dimeric bridging carbyne species.

##### 5.2 — REACTIONS OF COMPLEXES (C)

###### 5.2.1. WITH BASIC SOLVENTS

Dissolution of  $[|W(CNHMe)(dppe)_2|_2(\mu-CNHMe)_2]X_4$  (X =  $BF_4$ ,  $HSO_4$ ) (0.10g; 0.040 mmol) in pyridine (15 cm<sup>3</sup>) or in dimethylsulphoxide (15 cm<sup>3</sup>) followed by addition of benzene and concentration resulted in the precipitation of green *trans*- $[W(CNHMe)(CNMe)(dppe)_2]X$  (X =  $BF_4$ ; 0.050g, 0.043 mmol, 54% yield. X =  $HSO_4$ ; 0.060g, 0.052 mmol, 64% yield) or yellow  $[WH(CNMe)_2(dppe)_2]X$  (X =  $BF_4$ ; 0.055g, 0.048 mmol, 60% yield) respectively.

*trans*- $[W(CNHMe)(CNMe)(dppe)_2]X$  (X =  $BF_4$ ;

###### 5.2.2 — WITH METHANOL

Concentration of the solution, which resulted from MeOH (20 cm<sup>3</sup>) addition to  $[|W(CNHMe)(dppe)_2|_2(\mu-CNHMe)_2](BF_4)_4$  (0.15g, 0.061 mmol) followed by addition of ether led to the precipitation of pink *trans*- $[W(CNHMe)_2(dppe)_2](BF_4)_2$  (0.082g, 0.067 mmol, 55% yield).



5.2.3 — WITH THF/NaBPh<sub>4</sub>

NaBPh<sub>4</sub> (0.10g) was added to a thf (25 cm<sup>3</sup>) suspension of [W(CNHMe)(dppe)<sub>2</sub>](μ—CNHMe)<sub>2</sub> (BF<sub>4</sub>)<sub>4</sub> (0.13g, 0.053 mmol). The solid went into solution and [WH(CNHMe)(CNMe)(dppe)<sub>2</sub>] (BPh<sub>4</sub>)<sub>2</sub> (0.082g, 0.048 mmol, 35% yield) precipitated upon concentration.

 5.3 — DEALKYLATION OF *trans*-[M(CNMe)<sub>2</sub>(CNMe)(dppe)] BF<sub>4</sub> BY METHYL LITHIUM

Methyl lithium (4 cm<sup>3</sup> of a 2.3 M solution in ether; 9.2 mmol MeLi) was added to a suspension of *trans*-[M(CNMe)<sub>2</sub>(CNMe)(dppe)] (BF<sub>4</sub>) (M = Mo; 0.10g, 0.093 mmol; M = W; 0.13g, 0.11 mmol) in ether (15 cm<sup>3</sup>). After stirring overnight the colour of the suspension was reddish and the solid *trans*-[M(CNMe)<sub>2</sub>(dppe)] was separated, washed with ether, water, acetone and dried (M = Mo; 0.054g, 0.055 mmol, 60% yield; M = W; 0.077g, 0.073 mmol; 65% yield).

 5.4 — REACTIONS OF DIALKYLAMINOCARBYNE COMPLEXES WITH ACIDS  
PREPARATION OF POSSIBLE DIMERIC BRIDGED CARBYNE SPECIES (D)

## 5.4.1 — PREPARATION OF POSSIBLE BIS(μ—METHYLAMINOCARBYNE) BIS(DIMETHYLAMINOCARBYNE) TETRAKIS[1,2-BIS(DIPHENYLPHOSPHINO)ETHANE]DITUNGSTEN TETRAKIS(FLUOROBORATE OR FLUOROSULPHONATE)

Fluoroboric acid or fluorosulphonic acid (0.70 mmol, *i.e.*, 0.0969 or 0.0405 cm<sup>3</sup> respectively) was added to a suspension of green *trans*-[W(CNMe)<sub>2</sub>(CNMe)(dppe)] BF<sub>4</sub> (0.276g, 0.237 mmol) in thf (30 cm<sup>3</sup>) or in C<sub>6</sub>H<sub>6</sub> (15 cm<sup>3</sup>), respectively. The suspension colour immediately changed from green to yellow and after 0.5h the suspension was separated from the solution by filtration and washed by the solvent, giving the species formulated as [W(CNMe)<sub>2</sub>(dppe)<sub>2</sub>](μ—CNHMe)<sub>2</sub>X<sub>4</sub> (X = BF<sub>4</sub>; 0.291g, 98% yield. X = FSO<sub>3</sub> with one hydrogen-bonded HFSO<sub>3</sub> per monomeric unit; 0.319g, 98% yield).

## 5.4.2 — PREPARATION OF BIS(μ—METHYLAMINOCARBYNE) BIS(ETHYLMETHYLAMINOCARBYNE) TETRAKIS[1,2-BIS(DIPHENYLPHOSPHINO)ETHANE]DITUNGSTEN TETRAKIS(TETRAFLUOROBORATE)

Fluoroboric acid (0.030 cm<sup>3</sup>, 0.217 mmol) was added dropwise to a red solution of *cis*-[W(CNEtMe)(CNMe)(dppe)] BF<sub>4</sub> (0.300 g, 0.255 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>). Near the end of the addition, the solution colour faded and a yellow suspension of complex formulated as [W(CNEtMe)(dppe)<sub>2</sub>](μ—CNHMe)<sub>2</sub>(BF<sub>4</sub>)<sub>4</sub>·2CH<sub>2</sub>Cl<sub>2</sub> formed as fine needle crystals. It was separated from the solution by filtration and washed by ether (0.229 g, 71% yield).

## 5.5 — REACTIONS OF COMPLEXES (D)

## 5.5.1 — DEPROTONATION REACTIONS

Dissolution of [W(CNMe)<sub>2</sub>(dppe)]<sub>2</sub>(μ—CNHMe)<sub>2</sub>X<sub>4</sub> (X = BF<sub>4</sub>, FSO<sub>3</sub>) (0.15 g, 0.060 mmol) in pyridine (20 cm<sup>3</sup>), acetone (20 cm<sup>3</sup>) or thf (20 cm<sup>3</sup>) (upon addition of NaBPh<sub>4</sub>, 0.10 g) resulted in reddish solutions from which red *cis*-[W(CNMe)<sub>2</sub>(CNMe)(dppe)]X (X = BF<sub>4</sub>; *ca.* 40–60 mg, *ca.* 30–40% yield. X = FSO<sub>3</sub>; *ca.* 60–100 mg, *ca.* 40–70% yield) was obtained upon concentration and addition of benzene to pyridine and of ether to acetone or thf.

## 5.5.2 — REACTION WITH TRIFLUOROACETIC ACID

Preparation of *trans*-(methylaminocarbyne)(dimethylammoniumcarbyne)bis[1,2-bis(diphenylphosphino)ethane] tungsten tris(trifluoroacetate)

Addition of [W(CNMe)<sub>2</sub>(dppe)]<sub>2</sub>(μ—CNHMe)<sub>2</sub>(BF<sub>4</sub>)<sub>4</sub> (0.15 g, 0.060 mmol) to TFA (5 cm<sup>3</sup>) afforded a violet solution from which the violet solid *trans*-[W(CNMe)<sub>2</sub>(CNHMe)(dppe)] (CF<sub>3</sub>COO)<sub>3</sub> (E) was isolated upon concentration (0.15 g, 0.091 mmol, 76% yield).

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## RESUMO

Os complexos carbinicos  $[W(CNRMe)(CNMe)(dppe)_2]^+$  ( $R=H, Me$ ) no estado sólido (também em solução quando  $R=Me$ ) são susceptíveis de sofrer ataque protónico no átomo de azoto isonitrílico com formação de produtos formulados como complexos carbinicos em ponte  $[ \{ W(CNRMe)(dppe)_2 \} ]_2 (\mu -CNHMe)_2^{4+}$ , os quais sofrem, em solução, desprotonação e quebra da ponte.

A abstracção protónica ocorre em solventes básicos conduzindo à formação dos complexos progenitores, mas em ácido trifluoroacético o ligando carbinico  $CNMe_2$  sofre protonação no átomo de azoto com formação de trans- $[W(CNHMe)_2(CNHMe)(dppe)]^{3+}$ .

Na reacção de trans- $[Mo(CNMe)_2(CNMe)(dppe)]^+$  com LiMe resulta a desalquilação do ligando carbinico com formação do complexo progenitor bisisonitrílico.