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THE REACTIONS OF ISONITRILE COMPLEXES OF MOLYBDENUM(0) AND TUNGSTEN(0) WITH ALKYLATING AGENTS TO GIVE CARBYNE (AMINOMETHYNE) COMPLEXES

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Summary

Treatment of the complexes *trans*-$[M(CNMe)_2(dppe)_2]$ (A, M = Mo or W; dppe = $Ph_2PCH_2CH_2PPh_2$) with $MeFSO_3$, Me_2SO_4 or $[Et_3O]BF_4$ in benzene gives the complexes *trans*-$[M(CNRMe)(dppe)_2]X$ (B, R = Me or Et; X = FSO_3, $MeSO_4$ or BF_4). Dialkylated compounds were not observed. The compounds B isomerise in CH_2Cl_2 solution to give *cis*-$[M(CNRMe)(dppe)_2]X$. Spectroscopic data are reported for the complexes and are used to deduce their structures.

The complexes *trans*-$[M(CNR)_2(dppe)_2]$ (A, M = Mo or W; R = Me or t-Bu, dppe = $Ph_2PCH_2CH_2PPh_2$) can be protonated at the metal or at nitrogen to give hydride, carbene and carbyne complexes [1,2]. Here we report a similar study of the attack of the alkylating agents $MeFSO_3$, Me_2SO_4 and $[Et_3O]BF_4$ on compounds A, which leads to alkylation at nitrogen, but not at the metal.

Results and discussion

When treated with an excess of alkylating agent in benzene solution, complexes A rapidly give a precipitate of the bright green, monoalkylated compounds *trans*-$[M(CNRMe)(dppe)_2]X$ (R = Me or Et, X = FSO_3, $MeSO_4$ or BF_4) e.g. reaction 1.

trans-$[M(CNMe)_2(dppe)_2] + MeX \xrightarrow{C_6H_6}$

trans-$[M(CNMe_2)(CNMe)(dppe)_2]X$ . . . (1)

(M = Mo or W; X = FSO_3; M = W, X = $MeSO_4$)

Dialkylated species were never obtained even in the presence of up to 180 fold excess of alkylating agents.

We consider the attack of the alkylating agent to be at the nitrogen atom of complexes A by analogy with our protonation studies where such attack occurs

TABLE 1

PHYSICAL PROPERTIES OF MOLYBDENUM AND TUNGSTEN COMPLEXES [a]

	Colour	Yield (%)	M.p. (°C)	Analysis [b] C	H	N	ν(C≡N) [c] (cm^{-1})	(C=N) [c] (cm^{-1})	Λ_M [d] ($Scm^2\ mol^{-1}$)
trans-[Mo(CNMe$_2$)(CNMe)(dppe)$_2$]FSO$_3$	Green	93	232 (dec.)	62.8(62.8)	5.5(5.3)	2.6(2.6)	2180	1547	87
trans-[W(CNMe$_2$)(CNMe)(dppe)$_2$]FSO$_3$	Green	90	170 (dec.)	52.8(52.8)	5.1(4.9)	2.4(2.4)	2167	1552	88
trans-[W(CNMe$_2$)(CNMe)(dppe)$_2$]MeSO$_4$ [e]	Green	88	170—173	57.0(57.1)	5.3(5.0)	2.2(2.3)	2160	1547	81
cis-[Mo(CNMe$_2$)(CNMe)(dppe)$_2$]FSO$_3$ [f]	Red			62.5(62.9)	5.0(5.3)	2.5(2.6)	2070	1538	85
cis-[W(CNMe$_2$)(CNMe)(dppe)$_2$]FSO$_3$	Red	84	201—202	57.8(58.2)	4.8(4.8)	2.4(2.4)	2080	1545	84
cis-[W{CNEt(Me)}(CNMe)(dppe)$_2$]BF$_4$ [e]	Red	45	180—184	57.4(57.4)	5.0(5.0)	2.4(2.3)	2075	1537	88

[a] dppe = $Ph_2PCH_2CH_2PPh_2$. [b] Calculated values in parenthesis. [c] Nujol mulls. [d] In circa 10^{-3} *M* nitromethane solution unless otherwise stated. [e] contains 1/2 CH_2Cl_2 of crystallisation. [f] always mixed with *trans*-isomer in variable amount.

$$[R{-}N{\equiv}C \rightarrow \overset{+}{M}{\equiv}C{-}NR_2] \leftrightarrow [R{-}N{\equiv}C \rightarrow M{=}C{=}\overset{+}{N}R_2]$$

(a) (b)

Fig. 1.

unambiguously [1,2] and on the basis of the spectroscopic evidence described below. As we have already discussed [1,3] the very strong back donation which isonitriles receive from these metal centres causes a build-up of negative charge at isonitrile which can induce bending at the nitrogen atom and renders that atom susceptible to attack by electrophiles. Attack of this type has also been observed at isonitriles which bridge iron centres, giving such complexes as $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMeEt)]I$ [4]. The NMR equivalence over a wide temperature range of the $CNMe_2$ groups in our complexes, discussed below, confirms our assignment and eliminates the possibility of terminal iminoacyl ligands, C(R)NMe.

Analytical data etc. for these green, diamagnetic complexes are shown in Table 1. They conduct as 1 : 1 electrolytes in solvents such as nitromethane. In their solid state IR spectra they show a band for terminal isonitrile (C≡N stretching) in the region 2020—2170 cm^{-1}, some 230—300 cm^{-1} higher than in the parent complexes A. They also show a band in the region 1537—1552 cm^{-1} which is assigned to a (C=N) stretching vibration. The increase of ν(C≡N) relative to its value in complexes A, is expected since back donation to terminal isonitrile is necessarily decreased when the other isonitrile becomes a strong electron acceptor upon alkylation. The value of the lower frequency vibration indicates that in the description of the bonding shown in Fig. 1, canonical form (b) has a significant weight, as has been suggested in the analogous complexes $[MY(CNR_2)(CO)_4]$ (Y = Br or I, R = Me or Et) [5].

The FSO_3 salts showed IR absorptions characteristic of ionic fluorosulphate [6,7] at about 1285, 1065 and 585 cm^{-1} with a further band, expected at about 760 cm^{-1} obscured by dppe absorptions. Consistent with the ionic formulation, the ^{19}F NMR spectra of $[M(CNMe_2)(CNMe)(dppe)_2]FSO_3$ show only one single resonance in the range —299 to +239 ppm (39.0 ppm downfield from $CFCl_3$ for M = Mo, 38.9 ppm downfield for M = W, in $C^2H_2Cl_2$ solution). This chemical shift is close to that reported for $HFSO_3$ (—45.5 ppm in SO_2 solution) [8].

Complexes B do not show simple ^1H, ^{13}C or ^{31}P NMR spectra in solution, however. Moreover, they undergo a colour change from green to red on dissolution. Changes are also observed in their solution IR spectra when this colour change occurs which is interpreted as being due to *trans*- to *cis*-isomerisation. If reaction 1 is carried out in benzene as described above, the poorly soluble *trans*-complex may be isolated as a green precipitate. The complexes *trans*-$[M(CNHR)(CNR)(dppe)_2]^+$, isolated by a similar technique, are also green [1,2]. If, however, the green, *trans*-isomers are dissolved in a chlorinated solvent or in tetrahydrofuran (thf) an equilibrium is set up between them and the red *cis*-isomer which is clearly shown by NMR spectroscopy.

Spectroscopic properties and isomerisation

Both isomeric forms of the complexes exist in equilibrium in solution, the

TABLE 2

^{1}H NMR DATA FOR *trans*- AND *cis*-[M(CNRMe)(CNMe)(dppe)$_2$]X [a]

M	R	X	Temp. (°C)	δ (ppm) [b]	Integration [c]	Assignment
Mo	Me	FSO_3	25	7.8—7.6m		dppe
				6.39q [d]	2.4 (2.3) } 40 (40)	aromatic
				3.10s, br	2.8(3)	$CNCH_3$
				2.9—1.6m, br	8 (8)	dppe-CH_2
				2.20s	3.4 } 6 (7)	$CN(CH_3)_2$-*cis*
				2.10s	2.6	$CN(CH_3)_2$-*trans*
			−10	7.8—6.7m		dppe-
				6.31m [e]	2.3 (2.2) } 40 (40)	aromatic
				3.10s, br	2.9 (3)	$CNCH_3$
				2.16s	3.3 } 6 (6)	$CN(CH_3)_2$-*cis*
				2.11s	2.7	$CN(CH_3)_2$-*trans*
			−50	7.8—6.7m		
				6.32t [f]	1.1 } 40 (40)	dppe-
				6.10t [f]	11.1	aromatic
				3.10s, br	2.8 (3)	$CNCH_3$
				2.8—1.6m, br	8 (8)	dppe-CH_2
				2.11s	6 (6)	$CN(CH_3)_2$ both isomers
W	Me	FSO_3	25	7.8—6.7m		dppe-
				6.6—6.2m [g]	3.5 (3.5) } 40 (40)	aromatic
				3.21s, br	3 (3)	$CNCH_3$
				3.0—1.8m, br	8 (8)	dppe-CH_2
				2.21s	5.2 } 6 (6)	$CN(CH_3)_2$-*cis*
				2.17s	0.8	$CN(CH_3)_2$-*trans*

			−30	7.8—6.6m	} 40 (40)	dppe-
				6.40t [f]	1.5	aromatic
				6.15t [f]	1.5	
				3.20s, br	3 (3)	$CNCH_3$
				3.0—1.8m, br	8 (8)	dppe-CH_2
				2.15s	6 (6)	$CN(CH_3)_2$ both isomers
			−56	7.8—6.6m		
				6.37t [f]	1.1 (1) } 40 (40)	dppe-
				6.04t [f]	1.1 (1)	aromatic
				3.16s, br	3 (3)	$CNCH_3$
				2.9—1.8m, br	8 (8)	dppe-CH_2
				2.16s	3 } 6 (6)	$CN(CH_3)_2$-*trans*
				2.10s	3	$CN(CH_3)_2$-*cis*
			−70	7.8—6.6m		
				6.38t [f]	~0.7 (0.67) } 40 (40)	dppe-
				6.02t [f]	~0.7 (0.67)	aromatic
				3.13s, br	3(3)	$CNCH_3$
				3.1—1.8m, br	8 (8)	dppe-CH_2
				2.17s	4 } 6 (6)	$CN(CH_3)_2$-*trans*
				2.09s	2	$CN(CH_3)_2$-*cis*
W	Et	BF_4	25	7.8—6.6m	36 (36) }	dppe-
				6.30m [g]	4 (4)	aromatic
				3.21s, br	3 (3)	$CNCH_3$
				3.0—1.9m, br	10 (10)	dppe-CH_2 + $CN(CH_2CH_3)CH_3$
				2.0s	2.7 (3)	$CN(CH_2CH_3)CH_3$
				0.68t [h]	3 (3)	$CN(CH_2CH_3)CH_3$

[a] M = Mo or W; R = Me or Et, X = FSO_3 or BF_4. [b] In CH_2Cl_2 solution, relative to $SiMe_4$ ± 0.01. m = multiplet, q = quintet, s = singlet, br = broad. [c] Calculated values in parentheses. [d] Quartet (J = 8.0 ± 0.5 Hz) resulting from overlap of two triplets, (J = 8.0 Hz), *cis*-isomer (see text). [e] intermediate between 1 : 2 : 2 : 2 : 1 quintet and two triplets (*cis*-isomer). [f] J = 8.0 ± 0.5 Hz (*cis*-isomer). [g] 1 : 2 : 2 : 2 : 1 quintet from overlap of two triplets (J = 8.0 ± 0.5 Hz), *cis*-isomer. [h] J = 6.5 ± 0.5 Hz.

isomer distribution being temperature dependent. The most detailed study has been made for B (R = Me) and shows that at 25° C, the red *cis*-isomer predominates, but at lower temperatures the proportion of *trans*-isomer increases.

The assignment of the *cis*-structure follows from the observation of two phenyl triplets in the ^1H NMR spectra of B (R = Me) (Table 2) at low temperature, which overlap at higher temperatures. This triplet pattern has been observed as a characteristic resonance pattern in such complexes as *cis*-$[M(CO)_2(dppe)_2]$ (M = Cr, Mo or W) [9], and is assigned to the four *ortho*-phenyl protons of two phenyl rings, which interact with the two *cis*-non-phosphine ligands.

The ^{31}P spectrum confirms this assignment, the spectra at 25°C of $[M(CNMe_2)(CNMe)(dppe)_2]^+$ consist of a singlet for the *trans*-isomer and a more predominant complex pattern due to the *cis*-isomer. (Singlet at 89.5 ppm upfield from $P(OMe)_3$ for M = W; 70.7 ppm upfield for M = Mo). The ^1H NMR spectrum of $[W(CNMe_2)(CNMe)(dppe)_2]FSO_3$ shows at 25° C a singlet due to the $CNMe_2$ group in the *cis*-complex with a smaller resonance due to the *trans*-isomer (Table 2). On cooling to —70° C the *trans*-singlet grows at the expense of the *cis*-singlet, which also shifts to higher field with lowering of temperature (Table 2). At 25° C the integration ratios *trans* : *cis* are 0.75 and 0.14 (^{31}P spectrum) for Mo and W respectively, the corresponding ratios derived from the ^1H spectra being 0.76 and 0.15.

The ^{13}C NMR spectrum obtained for $[Mo(CNMe_2)(CNMe)(dppe)_2]FSO_3$ shows, at 25° C, two resonances (257.5 and 246.9 ppm downfield from $SiMe_4$) in the low field region associated with carbyne carbon. The lower field resonance is assigned to the *cis*-isomer since it has the highest intensity at this temperature. The chemical shift of the *trans*-isomer is close to that observed for its analogue *trans*-$[Mo(CNHMe)(CNMe)(dppe)_2]^+$ (247.8 ppm downfield) [2]. Two resonances are observed for the isonitrile carbon of $[Mo(CNMe_2)(CNMe)(dppe)_2]^+$, the less intense one is again assigned to that of the *trans*-isomer. Its chemical shift (160.6 ppm) is close to that observed for *C*NMe in $[Mo(CNHMe)(CNMe)(dppe)_2]^+$ (159.2 ppm). Two singlet resonances at 40.0 ppm and 38.7 ppm are tentatively assigned to $CN(CH_3)_2$ carbons of the two

TABLE 3

^{13}C NMR DATA FOR *cis*- AND *trans*-$[Mo(CNMe_2)(dppe)_2]FSO_3$

Position (ppm) [a]	Assignment
257.5m, br	$CNMe_2$(*cis*-isomer)
246.9m, br	$CNMe_2$(*trans*-isomer)
182.1m, br	*C*NMe (*cis*-isomer)
160.6m, br	*C*NMe (*trans*-isomer)
142.7—125.6m	dppe phenyls
40.0s, 38.7s [b]	$CN(CH_3)_2$ (*trans*-isomer)
	$CN(CH_3)_2$ (*cis*-isomer)
29.1—25.7m	$CNCH_3$ + dppe methylenes (*cis*- and *trans*-isomers)

[a] ppm downfield from internal $SiMe_4$ in $C^2H_2Cl_2$ solution at 25°C. The underlined value corresponds to the pre-eminent isomer. [b] Asymmetric quintet from overlap of two unequal intense quartets in off-resonanc continuous wave irradiation at δ = 10 (relative to $SiMe_4$). Apparent $^1J(CH)$ = 30.5 ± 1.5 Hz.

isomers. The $CNCH_3$ resonance overlaps with resonances due to the methylene carbons of dppe.

The IR spectra of the complexes (Table 1) also show the presence of two isomers and the assignments of Table 1 are based on the NMR assignments and by analogy with the green cations *trans*-$[M(CNHR)(CNR)(dppe)_2]^+$ [1,2]. Thus the green *trans*-isomers have higher values of $\nu(C{\equiv}N)$, in the range 2135—2180 cm^{-1}, compared to the red *cis*-isomer (2020—2070 cm^{-1}). The carbyne ligand appears to be more electron-withdrawing when *trans* to CNMe than is tertiary phosphine.

Conclusions

Alkylation of the nitrogen atom of ligating isonitrile has been established, but alkylation is not such a versatile process as is protonation. Whereas both nitrogen atoms in complexes A and also the metal can be protonated [1,2] alkylation only occurs at one nitrogen. The reasons for this difference may be steric but a wider variety of compounds must be studied to elucidate the factors involved in these processes.

Experimental

All reactions were carried out under dry dinitrogen and the solvents used were dried by standard techniques. The complexes *trans*-$[M(CNR)_2(dppe)_2]$ (A) were prepared by published methods [3]. Alkylating agents were used as commercially supplied (BDH). Infra-red spectra were recorded on a Perkin-Elmer 557 instrument and NMR spectra using a JEOL PS100 spectrometer equipped with a 564 J digital signal averager or on a JEOL PFT100 Fourier Transform Instrument. The solvents used for NMR spectroscopic studies were scrupulously dried, degassed and the solutions were prepared under vacuum directly in the NMR tubes which were then sealed in vacuo. Conductivities were measured with a Portland Electronics P310 conductivity bridge and uncorrected melting points with an Electrothermal melting point apparatus. Microanalyses were by Mr and Mrs Olney of these laboratories.

Preparation of dialkylaminocarbyne complexes from complexes A

Since preparations were general, representative examples of preparations are given below.

(a) Reactions with $MeFSO_3$, Preparation of trans-(dimethylaminocarbyne)-(methylisocyanide)bis[1,2-bis(diphenylphosphino)ethane]tungsten (or molybdenum)fluorosulphonate. Methylfluorosulphonate (0.147 cm^3, 1.86 mmol) was added dropwise to a stirred solution of *trans*-$[W(CNMe)_2(dppe)_2]$ (0.247 g, 0.233 mmol) in benzene (25 cm^3). Immediate formation of a shining green suspension occurred which after ca. 1 h was separated from the solution by filtration and was washed by benzene giving the analytically pure *trans*-$[W(CNMe_2)(CNMe)(dppe)_2]FSO_3$ as green needle crystals (0.245 g; 90% yield). The same experimental procedure affords the molybdenum dimethylaminocarbyne analogue.

The corresponding red *cis*-isomer (W) could be isolated by attempts to recrystallise the green *trans*-isomer from CH_2Cl_2 (red solution)/Et_2O.

(b) Reaction with dimethylsulphate. Preparation of trans-(dimethylaminocarbyne)(methylisocyanide)bis[1,2-bis(diphenylphosphino)ethane]tungsten methylsulphate. Dimethyl sulphate (2.04 cm^3, 21.5 mmol) was added to a dichloromethane solution (15 cm^3) of *trans*-$[W(CNMe)_2(dppe)_2]$ (0.127 g, 0.119 mmol). The solution, whose colour faded slightly, was left stirring overnight, concentrated and a green suspension of *trans*-$[W(CNMe_2)(CNMe)(dppe)_2]MeSO_4 \cdot \frac{1}{2} CH_2Cl_2$ (0.129 g; 88% yield) was isolated after addition of ether.

(c) Reaction with triethyloxonium fluoroborate. Preparation of cis-(ethylmethylaminocarbyne)(methyl isocyanide)bis[1,2-bis(diphenylphosphino)ethane]tungsten fluoroborate. Triethyloxonium fluoroborate (0.20 g, 1.05 mmol) was added to a solution of *trans*-$[W(CNMe)_2(dppe)_2]$ (0.404 g, 0.380 mmol) in CH_2Cl_2 (45 cm^3). The red solution colour darkened slightly. The solution was concentrated, methanol (30 cm^3) was added and a brick red precipitate was formed upon further concentration, which could be recrystallised from THF giving the red *cis*-$[W(CNEtMe)(CNMe)(dppe)_2]BF_4$ (0.202 g; 45% yield). Concentration of the mother liquor followed by addition of ether afforded the yellow complex *trans*-$[W(CNHMe)_2(dppe)_2](BF_4)_2$ [1,2] (0.188 g, 40% yield), probably formed by reaction of the parent complex with the protons liberated by reaction of methanol with the alkylating agent.

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