

ARENEDIAZO DERIVATIVES OF *o*-PHENYLENEBIS(DIMETHYLARSINE)-TETRACARBONYL-MOLYBDENUM AND -TUNGSTEN

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Summary

$[M(\text{das})(\text{CO})_4]$ and $[p\text{-RC}_6\text{H}_4\text{N}_2][\text{BF}_4]$ in CH_2Cl_2 yield the arenediazo complexes *mer*- $[M(\text{das})(\text{CO})_3(\text{N}_2\text{C}_6\text{H}_4\text{R-}p)][\text{BF}_4]$ (I: $M = \text{Mo}$, $R = \text{F}$; $M = \text{W}$, $R = \text{OMe}$) which react with halide ion to give $[M(\text{das})(\text{CO})_2\text{X}(\text{N}_2\text{C}_6\text{H}_4\text{R-}p)]$ ($M = \text{Mo}$, $R = \text{F}$, $\text{X} = \text{Cl}$ or I ; $M = \text{W}$, $R = \text{OMe}$, $\text{X} = \text{Cl}$, Br or I), and with $\text{Na}[\text{S}_2\text{CNMe}_2]$, $2 \text{H}_2\text{O}$ to give a mixture of $[\text{Mo}(\text{das})(\text{CO})(\text{N}_2\text{C}_6\text{H}_4\text{F-}p)(\text{S}_2\text{CNMe}_2)]$ and $[\text{Mo}(\text{N}_2\text{C}_6\text{H}_4\text{F-}p)_2(\text{S}_2\text{CNMe}_2)_2]$. Addition of chloride ions to the product of the reaction between I ($M = \text{Mo}$, $R = \text{F}$) and $\text{P}(\text{OMe})_3$ gives low yields of $[\text{Mo}(\text{das})(\text{CO})\text{Cl}\{\text{P}(\text{OMe})_3\}(\text{N}_2\text{C}_6\text{H}_4\text{F-}p)]$. The structures of the complexes have been determined by IR, ^1H and ^{13}C NMR spectroscopy allowing comparisons to be made with known arenediazo and nitrosyl analogues.

Introduction

Comparative studies of $[M(\text{L-L})(\text{CO})_3\text{Z}]^+$ ($M = \text{Mo}$ or W ; $\text{L-L} = \text{dppe}$ [1] *, *o*-phen or bipy [2]; $Z = \text{NO}$ or $\text{N}_2\text{C}_6\text{H}_4\text{R-}p$) have been hampered by the lack of definitive structural information. Recently [3] we have prepared $[M(\text{das})(\text{CO})_3(\text{NO})][\text{PF}_6]$ ($M = \text{Mo}$ and W) and their derivatives and unequivocally established their configurations by a combination of IR, ^1H and ^{13}C NMR spectroscopy. In addition the structures of *mer*- $[M(\text{L-L})(\text{CO})_3\text{Z}]^+$ ($M = \text{Mo}$ or W , $\text{L-L} = \text{dppe}$, $Z = \text{NO}$; $M = \text{W}$, $\text{L-L} = \textit{o}$ -phen, $Z = \text{NO}$) and *fac*- $[M(\text{L-L})(\text{CO})_3\text{Z}]^+$ ($M = \text{Mo}$, $\text{L-L} = \text{bipy}$, $Z = \text{NO}$ or $\text{N}_2\text{C}_6\text{H}_4\text{R-}p$) have been determined by ^{31}P NMR spectroscopy or by inference. We now report the structural characterisation of *mer*- $[M(\text{das})(\text{CO})_3(\text{N}_2\text{C}_6\text{H}_4\text{R-}p)]^+$ ($M = \text{Mo}$ and W), and of their derivatives, and

(Continued on p-182)

* Abbreviations used: dppe, bis(diphenylphosphino)ethane; *o*-phen, *ortho*-phenanthroline; bipy, 2,2'-bipyridyl; das, *ortho*-phenylenebis(dimethylarsine); dmpe, bis(dimethylphosphino)ethane; dcpe, bis(dicyclohexylphosphino)ethane.

TABLE 1
ANALYTICAL AND IR DATA FOR ARENE DIAZO COMPLEXES OF *o*-PHENYLENEBIS(DIMETHYLARSINE) SUBSTITUTED GROUP VI METAL
CARBONYLS

Complex	Colour	Yield (%)	Analyses Found (calcd.) (%)			IR data (cm ⁻¹) ^a	
			C	H	N	$\nu(\text{CO})$ ^b	$\nu(\text{NN})$
[W(das)(CO) ₃ (N ₂ C ₆ H ₄ OMe- <i>p</i>)] [BF ₄]	dark brown	95	31.1 (31.0)	3.1 (3.0)	3.8 (3.6)	2062m, 1991(sh), 1964s	1686m ^b
[Mo(das)(CO) ₂ Cl(N ₂ C ₆ H ₄ F- <i>p</i>)]	red brown	19	36.8 (36.2)	3.5 (3.4)	4.8 (4.7)	2020, 1948	1543
[W(das)(CO) ₂ Cl(N ₂ C ₆ H ₄ OMe- <i>p</i>)]	dark green	49	32.6 (32.8)	3.3 (3.3)	4.0 (4.0)	2003, 1923	1548
[W(das)(CO) ₂ Br(N ₂ C ₆ H ₄ OMe- <i>p</i>)]	dark green	42	31.0 (30.8)	3.3 (3.1)	3.9 (3.8)	2003, 1923	1547
[W(das)(CO) ₂ (N ₂ C ₆ H ₄ OMe- <i>p</i>)]	dark green	59	29.4 (29.0)	3.0 (2.9)	3.5 (3.5)	2003, 1925	1543
[Mo(das)(CO)(N ₂ C ₆ H ₄ F- <i>p</i>)(S ₂ CNMe ₂)]	orange	24	37.3 (36.8)	4.2 (4.0)	6.5 (6.4)	1854	1524
[Mo(N ₂ C ₆ H ₄ F- <i>p</i>) ₂ (S ₂ CNMe ₂) ₂]	purple	7	37.3 (37.1)	3.7 (3.5)	13.6 (14.4)	—	^d
[Mo(das)(CO)Cl{P(OMe) ₃ }(N ₂ C ₆ H ₄ F- <i>p</i>)]	red	1	34.8 (34.7)	4.2 (4.2)	3.7 (4.0)	1920	1527

^a All the absorptions are strong unless otherwise stated (m, medium; s, strong; sh, shoulder). ^b In CH₂Cl₂. ^c In Nujol unless otherwise stated. ^d Obscured by sulphur ligand vibrations.

TABLE 2

 ^1H NMR DATA ^a FOR ARENEDIAZO COMPLEXES OF *o*-PHENYLENEBIS(DIMETHYLARSINE) SUBSTITUTED GROUP VI METAL CARBOONYLS

Complex	<i>o</i> -Phenylenebis(dimethylarsine) resonances		Arenediazo ring protons	Other protons
	Ring protons	Methyl protons		
[W(das)(CO) ₃ (N ₂ C ₆ H ₄ OMe- <i>p</i>)] [BF ₄]	2.12(4, m)	7.75(6, s), 7.96(6, s)	2.72(4, m)	6.07(3, s, OMe)
[Mo(das)(CO) ₂ Cl(N ₂ C ₆ H ₄ F- <i>p</i>)]	2.22(4, [AB] ₂)	8.21(6, s), 8.33(6, s)	2.95(4, d)	—
[W(das)(CO) ₂ Cl(N ₂ C ₆ H ₄ OMe- <i>p</i>)]	2.14(4, [AB] ₂)	8.13(6, s), 8.26(6, s)	3.03(4, s)	6.20(3, s, OMe)
[W(das)(CO) ₂ Br(N ₂ C ₆ H ₄ OMe- <i>p</i>)]	2.27(4, [AB] ₂)	8.10(6, s), 8.33(6, s)	3.13(4, s)	6.25(3, s, OMe)
[W(das)(CO) ₂ (N ₂ C ₆ H ₄ OMe- <i>p</i>)]	2.16(4, [AB] ₂)	7.90(6, s), 8.28(6, s)	2.98(4, d)	6.18(3, s, OMe)
[Mo(das)(CO)(N ₂ C ₆ H ₄ F- <i>p</i>)(S ₂ CNMe ₂)]	ca. 2.5 (4, m) ^b	8.10(3, s), 8.27(3, s), 8.33(3, s), 8.56(3, s)	ca. 2.5 (4, m) ^b	6.51(3, s, Me), 6.70(3, s, Me)
[Mo(N ₂ C ₆ H ₄ F- <i>p</i>) ₂ (S ₂ CNMe ₂) ₂]	—	—	2.72(4, m)	6.54(6, s, Me), 6.62(6, s, Me)

^a In CD₃NO₂ unless otherwise stated. Intensity and multiplicity in parentheses (s, singlet; d, doublet; m, multiplet). ^b Uncertain because of signal coincidence.

make comments on the relative reactivities of the nitrosyl and arenediazo complexes $[M(L-L)(CO)_3Z]^+$.

Results and discussion

The reaction between $[M(das)(CO)_4]$ ($M = Mo$ or W) and arenediazonium salts, $[p-R_1C_6H_4N_2][BF_4]$ ($R = F, OMe, \text{ or } NO_2$), in CH_2Cl_2 affords dark brown solutions which contain $[M(das)(CO)_3(N_2C_6H_4R-p)][BF_4]$ (I). For $M = W$, $R = OMe$ the product was isolated as a dark brown solid and fully characterised (Tables 1 and 2) as a 1/1 electrolyte ($\Lambda_m = 150 \text{ s cm}^2 \text{ mol}^{-1}$, $10^{-4} M$ in acetone). The carbonyl IR spectrum is similar to those of the nitrosyl complexes $[M(L-L)(CO)_3(NO)][PF_6]$ ($M = Mo$ or W , $L-L = das$ [3], *dppe* [1], *dmpe*, or *dcpe* [4]; $M = W$, $L-L = o\text{-phen}$ [2]) to which we have assigned [3] the *mer*-geometry; the 1H NMR (Table 1) and proton-decoupled ^{13}C NMR (in CH_2Cl_2 ; 14.8, 15.6 (C(14,15)); 56.2 (C(13)); 116.1 (C(12)); 123.6 (C(11)); 131.4, 131.6, 133.1, 133.4 (C(7-10)); 136.5 (C(6)); 139.0; 139.5 (C(4,5)); 162.0 (C(3)); 195.5 C(2)); 207-209 (C(1)), in ppm, downfield from tetramethylsilane) confirm that I ($M = W$, $R = OMe$) is isostructural (Fig. 1). Although other examples of I could not be isolated for full characterisation $[p-NO_2C_6H_4N_2][BF_4]$ reacts with $[W(das)(CO)_4]$ in CH_2Cl_2 to give initially I ($M = W$, $R = NO_2$), identified by its IR carbonyl spectrum ($\bar{\nu}(CO)$ 2070m, 2001(sh), and 1978s cm^{-1}). Over prolonged periods decomposition occurs via a complex which shows only two carbonyl bands, of similar intensity, at 2021 and 1949 cm^{-1} . It is noteworthy that the reaction of diazonium salts with $[Mo(L-L)(CO)_4]$ ($L-L = o\text{-phen}$ and *bipy*) affords [2] the *fac*-isomer of $[Mo(L-L)(CO)_3(N_2C_6H_4R-p)]^+$ which has a similar carbonyl spectrum. It may be tentatively suggested that *mer*- $[W(das)(CO)_3(N_2C_6H_4OMe-p)]^+$ isomerises to the *fac*-isomer and that although *fac*- $[Mo(L-L)(CO)_3(N_2C_6H_4R-p)][BF_4]$ has been isolated the *mer*-isomers are initially formed. In support of this suggestion both *fac*- $[Mo(L-L)(CO)_3(NO)][BF_4]$ ($L-L = o\text{-phen}$ or *bipy*) and *mer*- $[W(o\text{-phen})(CO)_3(NO)][PF_6]$ are known [2].

$[Mo(das)(CO)_4]$ also reacts with arenediazonium salts to give solutions of I ($M = Mo$). Although $[Mo(das)(CO)_3(N_2C_6H_4F-p)]^+$ ($\bar{\nu}(CO)$ 2073m, 2010(sh), and 1983s cm^{-1} ; $\bar{\nu}(NN)$ 1692ms cm^{-1} (in CH_2Cl_2)) has not been isolated it may be generated in solution essentially free from other carbonyl-containing species. Such solutions have been used in the synthesis of derivatives described below.

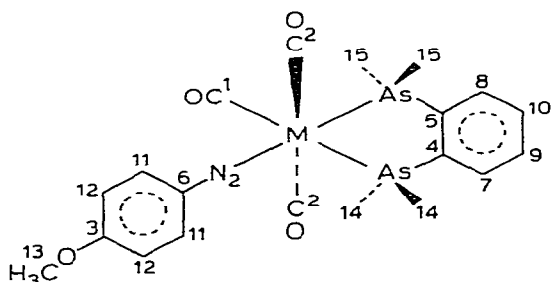


Fig. 1.

[Mo(das)(CO)₄] and [*p*-MeOC₆H₄N₂][BF₄] give a mixture of carbonyl-containing products in CH₂Cl₂ including I (M = Mo, R = OMe) ($\bar{\nu}(\text{CO}) = 2065\text{m}$, 2013sh, and 1977s cm⁻¹).

The complexes I (M = W, R = OMe) and I (M = Mo, R = F) undergo a limited range of substitution reactions which, however, generally parallel those of the nitrosyl analogues [M(das)(CO)₃(NO)][PF₆] (M = Mo or W) [3]. Addition of [AsPh₄]Cl to I (M = Mo, R = F) in CH₂Cl₂ rapidly yields red-brown solutions from which [M(das)(CO)₂X(N₂C₆H₄R-*p*)] (II) (M = Mo, X = Cl, R = F) may be isolated and fully characterised (Tables 1 and 2). The observation of two carbonyl bands, of equal intensity, in the IR spectrum, and the ¹H NMR spectrum (Table 2), which has only two das-methyl resonances and an [AB]₂ pattern for the *o*-phenylene ring protons, show II (X = Cl, R = F) (Fig. 2) to be isostructural with [M(das)(CO)₂X(NO)] (M = Mo or W; X = Cl, Br or I) [3]. The mechanism of formation of II from I is therefore likely to be the same as for the halonitrosyl complexes with initial displacement of the arsenic atom *trans* to N₂C₆H₄R-*p*, giving [M(das)(CO)₃X(N₂C₆H₄R-*p*)], followed by carbonyl displacement and chelation of das.

The structure established for II is also probably adopted by [Mo(L-L)(CO)₂X(N₂C₆H₄R-*p*)] (L-L = *o*-phen or bipy, R = Me or F) [2]. Whereas the carbonyl stretching frequencies of the das complex are higher than those of the nitrogen chelate analogues, as expected if the carbonyls are *trans* to L-L, $\bar{\nu}(\text{NN})$ is essentially invariant.

The reaction between I (M = W, R = OMe) and halide ion is more complex than that with molybdenum. Addition of [PMePh₃]I to I in CHCl₃ gave a solution containing two *cis*-dicarbonyl complexes (A: $\bar{\nu}(\text{CO})$ 2061 and 2003 cm⁻¹; B: $\bar{\nu}(\text{CO})$ 2003 and 1925 cm⁻¹) but after two weeks only those absorptions due to A were apparent. On column chromatography (alumina/CH₂Cl₂), however, only B was isolated. Similar results were obtained with chloride or bromide although complete conversion to the analogue of A did not occur. The identity of B as [W(das)(CO)₂I(N₂C₆H₄OMe-*p*)], isostructural with II (M = Mo, X = Cl, R = F) (Fig. 2), follows from the carbonyl IR (Table 1) and ¹H NMR spectra (Table 2). The nature of A, however, is unknown. Attempts to isolate A by methods other than column chromatography were hampered by the presence of highly coloured impurities, probably arsine analogues of [R₃P-N=N-Ar]⁺ which result from the reaction between phosphines and diazonium salts [5]. The formation of A from B does not involve a simple isomerisation process since pure B does not convert to A in solution. Similarly excess iodide ion is not involved as pure B and [PMePh₃]I do not react in CHCl₃. The addition of [*p*-MeOC₆H₄N₂][BF₄] to B in CH₂Cl₂ does, however, give A suggesting that free diazonium ion, formed in the reaction between I and halide ion, is involved in the process. Although

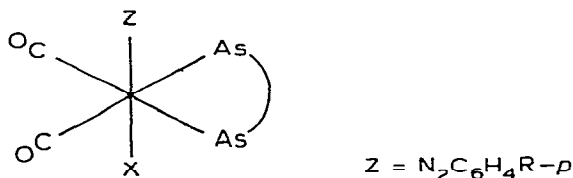


Fig. 2

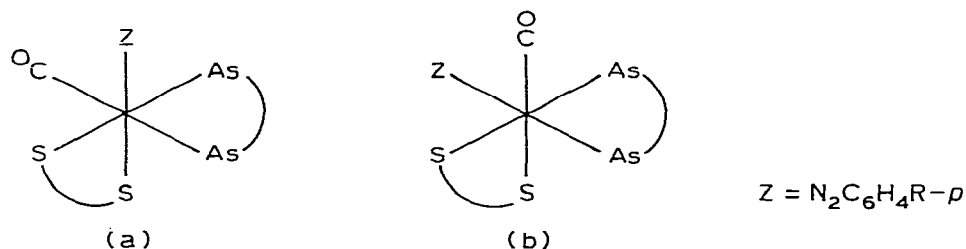


Fig. 3

diazonium ions act as weak one-electron oxidants towards transition metal complexes [6], preliminary cyclic voltammetric studies indicate that B does not readily undergo one-electron oxidation. The high frequencies of the carbonyl absorptions of A, relative to B, suggest that the former is positively charged, possibly an adduct $[\text{W}(\text{das})(\text{CO})_2\text{I}(\text{N}_2\text{C}_6\text{H}_4\text{OMe}-p)_2]^+$ either containing a monodentate das ligand or one "bent" and one "doubly-bent" [7], formally $[\text{N}_2\text{C}_6\text{H}_4\text{OMe}-p]^-$ ligand.

The reaction between I ($M = \text{W}$, $R = \text{OMe}$) and $\text{Na}[\text{S}_2\text{CNMe}_2] \cdot 2\text{H}_2\text{O}$ in acetone gave a mixture of products which could not be characterised. With a solution of I ($M = \text{Mo}$, $R = \text{F}$), however, the dithiocarbamate ion gave orange $[\text{Mo}(\text{das})(\text{CO})(\text{N}_2\text{C}_6\text{H}_4\text{F}-p)(\text{S}_2\text{CNMe}_2)]$ (III) and purple $[\text{Mo}(\text{N}_2\text{C}_6\text{H}_4\text{F}-p)_2(\text{S}_2\text{CNMe}_2)_2]$ (IV) separable by column chromatography. The ^1H NMR spectrum of III (Table 2) shows two methyl resonances for the sulphur ligand and four for das, ruling out a *trans*-carbonylarenediazo structure but not distinguishing between a and b (Fig. 3). It is interesting to note that the nitrosyl analogue of III was prepared as a mixture of both of the *cis*-isomers.

Complex IV is a rare example of a bis-arenediazo complex. Although many dinitrosyls are known only $[\text{RuCl}(\text{PPh}_3)_2(\text{N}_2\text{C}_6\text{H}_4\text{R})_2]^+$ [8], $[\text{Mn}(\text{CO})(\text{PPh}_3)_2(\text{N}_2\text{Ph})_2]^+$, $[\text{Mn}(\text{CO})\text{X}(\text{PPh}_3)_2(\text{N}_2\text{Ph})_2]$ ($\text{X} = \text{Cl}$, Br , or NCO) [9] and $[\text{Mo}(\text{PPh}_3)_2(\text{N}_2\text{Ph})_2\text{Cp}]^+$ [10] have been reported previously. The mass spectrum of IV shows a parent ion and the sequential loss of the two arenediazo ligands. Unfortunately $\bar{\nu}(\text{NN})$ cannot be determined from the IR spectrum due to overlap with absorptions associated with the CN bond of the dithiocarbamate ligand. The ^1H NMR spectrum, however, shows two methyl resonances (Table 2) and therefore that IV has a *cis*-configuration related to that of $[\text{Mo}(\text{NO})_2(\text{S}_2\text{CNR}_2)_2]$ [11].

Whereas I ($M = \text{W}$, $R = \text{OMe}$) reacts with $\text{P}(\text{OMe})_3$ or PPh_3 to give a mixture of uncharacterised products, addition of $\text{P}(\text{OMe})_3$ to a solution of I ($M = \text{Mo}$, $R = \text{F}$) in CH_2Cl_2 , followed by reaction of the product with chloride ion gave very low yields of $[\text{Mo}(\text{das})(\text{CO})\text{Cl}\{\text{P}(\text{OMe})_3\}(\text{N}_2\text{C}_6\text{H}_4\text{F}-p)]$. The complex was characterised by elemental analysis, IR spectroscopy (Table 1) and its mass spectrum which showed a parent ion and sequential loss of the carbonyl and four methyl groups.

Conclusion

Although I undergoes a limited range of substitution reactions they appear to parallel those of previously reported nitrosyl and arenediazo analogues

$[M(L-L)(CO)_3Z]^+$ ($M = Mo$ or W ; $L-L = dppe$, *o*-phen, or bipy; $Z = NO$ or $N_2C_6H_4R-p$). The spectral studies reported show that complexes which differ only in the chelate ligand $L-L$ are isostructural suggesting that the course of the substitution reactions is essentially the same; the stereochemistry of the products appears to depend on the *trans*-labilising abilities of the strong π -accepting nitrosyl and arenediazo ligands. Throughout the chemistry of the six-coordinate complexes $[M(L-L)(CO)_3Z]^+$, and of their derivatives, isomerisation is surprisingly common. Again the *trans*-labilising ability of Z may well result in the formation of readily isomerised five-coordinate intermediates.

Experimental

The preparation and purification of the complexes described were carried out under an atmosphere of dry nitrogen. Unless otherwise stated the complexes are moderately air-stable in the solid state and dissolve in polar solvents such as acetone and CH_2Cl_2 to give solutions which slowly decompose in air. $[W(das)(CO)_4]$ [12] and $[p-RC_6H_4N_2][BF_4]$ [13] were prepared by published methods.

IR spectra were recorded on Perkin-Elmer PE257 or PE457 spectrophotometers and calibrated against the absorption of polystyrene at 1601 cm^{-1} . 1H NMR spectra were recorded on Varian Associates HA100 or JEOL PS100 instruments, ^{13}C NMR spectra on a Jeol PFT 100 spectrometer, and mass spectra on an A.E.I. MS9 instrument. Microanalyses were by the Microanalytical Service of the School of Chemistry, University of Bristol.

{o-Phenylenebis(dimethylarsine)} tricarbonyl(p-methoxybenzenediazo) tungsten tetrafluoroborate $[W(das)(CO)_3(N_2C_6H_4OMe-p)][BF_4]$

$[W(das)(CO)_4]$ (0.90 g, 1.55 mmol) and $[p-MeOC_6H_4N_2][BF_4]$ (1.80 g, 8.11 mmol) were stirred in CH_2Cl_2 (120 cm^3) until the carbonyl absorptions of the starting material were absent from the IR spectrum (ca. 16 h). The brown solution was filtered, evaporated to low volume (ca. 15 cm^3) and added to an excess of diethyl ether (80 cm^3). Storage at $0^\circ C$ gave dark brown $[W(das)(CO)_3(N_2C_6H_4OMe-p)][BF_4]$, yield 1.13 g (95% based on $[W(das)(CO)_4]$).

{o-Phenylenebis(dimethylarsine)} dicarbonylchloro(p-methoxybenzenediazo) tungsten $[W(das)(CO)_2Cl(N_2C_6H_4OMe-p)]$

$[W(das)(CO)_3(N_2C_6H_4OMe-p)][BF_4]$ (0.40 g, 0.52 mmol) and $[AsPh_4]Cl$ (0.23 g, 0.55 mmol) were stirred in $CHCl_3$ (70 cm^3) until the carbonyl absorptions of the starting material were absent from the IR spectrum (ca. 10 min). The dark green solution was evaporated to dryness and the residue chromatographed on alumina/ CH_2Cl_2 . The yellow-green band was eluted with CH_2Cl_2 to give a green solution which, on addition of hexane and partial evaporation, gave dark green crystals of $[W(das)(CO)_2Cl(N_2C_6H_4OMe-p)]$, yield 0.18 g (49%).

$[W(das)(CO)_2X(N_2C_6H_4OMe-p)]$ ($X = Br$ or I) were prepared by similar methods.

{o-phenylenebis(dimethylarsine)} dicarbonylchloro(p-fluorobenzenediazo) molybdenum $[Mo(das)(CO)_2Cl(N_2C_6H_4F-p)]$

$[Mo(das)(CO)_4]$ (0.60 g, 1.21 mmol) and $[p-FC_6H_4N_2][BF_4]$ were stirred

in CH_2Cl_2 (75 cm^3) until the carbonyl absorptions of $[\text{Mo}(\text{das})(\text{CO})_4]$ were absent from the IR spectrum (ca. 90 min). The brown solution was then filtered and $[\text{AsPh}_4]\text{Cl}$ (0.71 g, 1.69 mmol) added. After stirring for about 10 min only two carbonyl bands were present in the IR spectrum. The red-brown solution was then filtered and evaporated to dryness. Treatment of the residue as for the tungsten complex (see above) gave red-brown crystals of $[\text{Mo}(\text{das})(\text{CO})_2\text{-Cl}(\text{N}_2\text{C}_6\text{H}_4\text{F-}p)]$, yield 0.14 g (19% based on $[\text{Mo}(\text{das})(\text{CO})_4]$).

Reaction of $[\text{Mo}(\text{das})(\text{CO})_4]$ with $[p\text{-FC}_6\text{H}_4\text{N}_2][\text{BF}_4]$ and $\text{Na}[\text{S}_2\text{CNMe}_2], 2\text{H}_2\text{O}$

$[\text{Mo}(\text{das})(\text{CO})_4]$ (0.95 g, 1.92 mmol) and $[p\text{-FC}_6\text{H}_4\text{N}_2][\text{BF}_4]$ (0.95 g, 4.52 mmol) were stirred in CH_2Cl_2 (70 cm^3) for 90 min. After filtration $\text{Na}[\text{S}_2\text{CNMe}_2] \cdot 2\text{H}_2\text{O}$ (0.35 g, 1.96 mmol) was added to the brown solution, and stirring was continued for 8½ h. The reaction mixture was then evaporated to dryness and the residue chromatographed on alumina/ CH_2Cl_2 (50%)/hexane (50%) to afford purple, orange, and scarlet-red bands. Elution of the purple band with 1/1 CH_2Cl_2 /hexane gave a purple solution from which purple crystals of $[\text{Mo}(\text{N}_2\text{C}_6\text{H}_4\text{F-}p)_2(\text{S}_2\text{CNMe}_2)_2]$ were obtained by addition of hexane, yield 0.08 g (7% based on $[\text{Mo}(\text{das})(\text{CO})_4]$). Elution of the orange band with CH_2Cl_2 gave an orange solution from which $[\text{Mo}(\text{das})(\text{CO})(\text{N}_2\text{C}_6\text{H}_4\text{F-}p)(\text{S}_2\text{CNMe}_2)]$ was obtained by addition of hexane and partial evaporation, yield 0.30 g (24% based on $[\text{Mo}(\text{das})(\text{CO})_4]$). The remaining scarlet-red band could not be removed from the column.

$[\text{Mo}(\text{das})(\text{CO})(\text{N}_2\text{C}_6\text{H}_4\text{F-}p)(\text{S}_2\text{CNMe}_2)]$ dissolves in most common organic solvents to give orange solutions which slowly decompose in air.

{o-Phenylenebis(dimethylarsine)} carbonylchloro(trimethylphosphite)(p-fluorobenzenediazo)molybdenum $[\text{Mo}(\text{das})(\text{CO})\text{Cl}\{\text{P}(\text{OMe})_3\}(\text{N}_2\text{C}_6\text{H}_4\text{F-}p)]$

$[\text{Mo}(\text{das})(\text{CO})_4]$ (0.50 g, 1.01 mmol) and $[p\text{-FC}_6\text{H}_4\text{N}_2][\text{BF}_4]$ (0.50 g, 2.38 mmol) were stirred in CH_2Cl_2 (60 cm^3) for ca. 90 min. After filtration, $\text{P}(\text{OMe})_3$ (0.14 g, 1.13 mmol) was added to the brown solution and the mixture was stirred for a further 260 min. $[\text{AsPh}_4]\text{Cl}$ (0.35 g, 0.83 mmol) was then added and after stirring for 10 min the solution was evaporated to dryness. The residue was then chromatographed on alumina/ CH_2Cl_2 and elution of the yellow band gave a yellow solution. Further bands could not be removed from the column. Addition of hexane to the yellow solution and cooling to 0°C gave red crystals of $[\text{Mo}(\text{das})(\text{CO})\text{Cl}\{\text{P}(\text{OMe})_3\}(\text{N}_2\text{C}_6\text{H}_4\text{F-}p)]$ yield 8 mg {1% based on $[\text{Mo}(\text{das})(\text{CO})_4]$ }.

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