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REACTIONS OF COORDINATED NITRIDE TO GENERATE NOVEL RHENIUM AND MOLYBDENUM IMIDO COMPLEXES: THE CRYSTAL AND MOLECULAR STRUCTURES OF $[Mo(NCPh_3)(S_2CNMe_2)_3]BF_4$ AND $[Mo(NSO_2Ph)(S_2CNMe_2)_3]PF_6$ *

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Summary

The nitrido complexes $[MoN(S_2CNR_2)_3]$ (R_2 = Me_2, Et_2) and $[ReN(S_2CNR_2)_2(PMe_2Ph)_n]$ (R_2 = Me_2; Et_2; n = 0, 1) react with halides R'X (R' = PhCO, $PhSO_2$, 2,4-$(NO_2)_2C_6H_3$, 2,4-$(NO_2)_2C_6H_3S$; X = Cl, R' = Me, X = I), $[R'_3O]BF_4$ (R' = Me, Et) or $[Ph_3C]BF_4$ to give the imido complexes $[Mo(NR')(S_2CNR_2)_3]^+$ and $[Re(NR')(S_2CNR_2)_2(PMe_2Ph)_n]$ (R' = Me, Et, Ph_3C^+, $PhSO_2$, PhCO, 2,4$(O_2N)_2C_6H_3$, 2,4-$(O_2N)_2C_6H_3S$); the X-ray crystal structures of $[Mo(NCPh_3)(S_2CNMe_2)_3]BF_4$ and $[Mo(NSO_2Ph)(S_2CNMe_2)_3]PF_6$ have been determined. Both complexes have approximately pentagonal bipyramidal geometries although the NSO_2Ph complex is more distorted. The $NCPh_3$ and NSO_2Ph complexes have Mo—N—C and Mo—N—S angles of 175.1(5)° and 161.3(13)° and Mo—N distances of 1.731(2) and 1.70(2)Å, respectively.

Recent EXAFS studies of nitrogenase [1] and its iron-molybdenum cofactor [2] indicate strongly that the molybdenum is in a cluster environment involving iron and sulphur. The molybdenum is generally recognised as the most probable candidate for the active site of the enzyme. We have attempted to generate a sulphur environment for molybdenum using dithiocarbamates and we have explored the chemistry of some dithiocarbamato-nitrido complexes. Nitrides are important as probable intermediates in both the fixation of nitrogen by early transition metals on reduction and the protic degradation of coordinated dinitrogen to ammonia. A knowledge of the chemistry of metal nitrido

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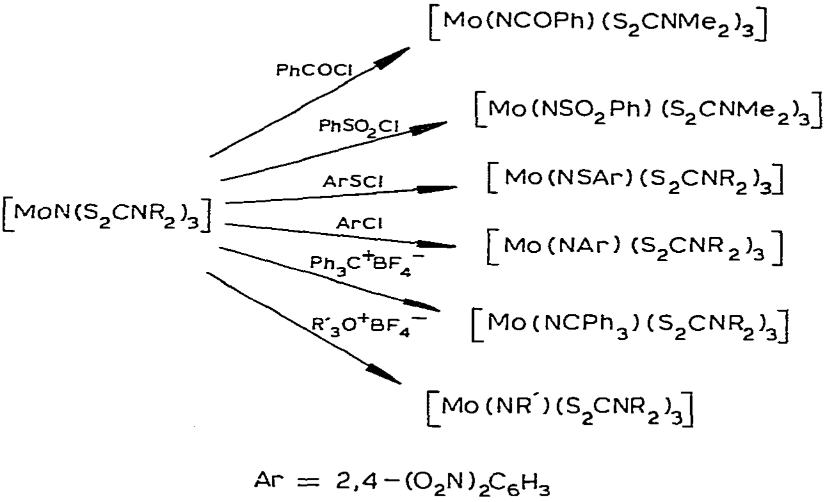
* Dedicated to the memory of Professor Paolo Chini.

complexes will greatly assist the understanding of the above nitrogen fixation processes. Here we report the full details [3] of the preparation and characterisation of a range of molybdenum and rhenium imido complexes by reaction of the nitrides $[MoN(S_2CNR_2)_3]$ ($R_2 = Me_2$, Et_2, $(CH_2)_5$) or $[ReN(S_2CNR_2)_2(PMe_2Ph)_n]$ ($n = 0$ or 1; $R_2 = Me_2$, Et_2) with electrophilic reagents.

The formation of thionitrosyl complexes by the cleavage of elemental sulphur [4] suggested that the nitride ligand in the complexes $[MoN(S_2CNR_2)_3]$ was very nucleophilic. Indeed the nitrido complexes react rapidly with a range of electrophiles to generate imido complexes with N—C or N—S bonds as shown in Scheme 1. Some rhenium imido complexes could be prepared in analogous manner as shown in eqs. 1 and 2.



SCHEME 1.THE REACTIONS OF $[MoN(S_2CNR_2)_3]$ WITH ELECTROPHILIC REAGENTS

$$[ReN(S_2CNMe_2)_2(PMe_2Ph)] + Ph_3\overset{+}{C}BF_4^- \rightarrow [Re(NCPh_3)(S_2CNMe_2)_2(PMe_2Ph)]BF_4 \quad (1)$$

$$[ReN(S_2CNMe_2)_2(PMe_2Ph)] + ArSCl \rightarrow [Re(NSAr)(S_2CNMe_2)_2(PMe_2Ph)]Cl \quad (2)$$

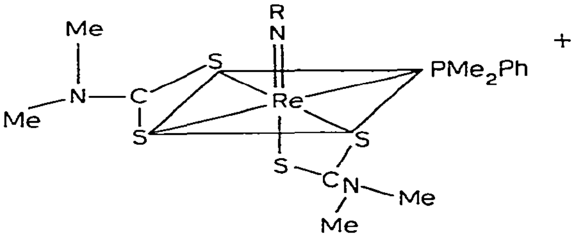
$Ar = 2,4\text{-}(O_2N)_2C_6H_3$

The complexes thus prepared are summarised in Table 1, together with analytical and spectroscopic data.

Although $[MoN(S_2CNMe_2)_3]$ reacted with methyl iodide to give an alkylimido complex, no reaction occurred with the rhenium nitrides. Arylimido complexes could only be obtained by use of the activated halide 2,4-dinitrochlorobenzene. The 2,4-dinitrophenylsulphenylimido complexes could be prepared either by reaction of a thionitrosyl complex with 2,4-dinitrochlorobenzene. The lack of suitable nitride precursors prevents these preparative routes being of general application to obtain imido complexes. Nevertheless it does permit the preparation of imido complexes which would be extremely difficult to derive by other routes.

Considering the molybdenum complexes first; the low conductivity values found for complexes XIII, XIV, and XVI suggested initially that these may be non-electrolytes. However the similarity of their ^{1}H NMR spectra to the species with non-coordinating anions suggested that all the molybdenum complexes have the same seven-coordinate pentagonal bipyramidal structure. The ^{1}H NMR spectra are generally rather uninformative with imido-proton resonances frequently obscured by ligand bands.

In the case of rhenium the complexes VIII and IX probably have structure analogous to the square pyramidal nitride precursor. However the somewhat low conductivities suggest the possibility of interaction of the BF_4^- anion at the vacant site *trans* to the nitride ligand. The ^{1}H NMR spectra of complexes X and XI suggest the geometry shown below.



The resonances due to the methylimido ligand in complex XI are split into a doublet due to coupling with the *cis* PMe_2Ph ligand. The observation of a pair of doublets for the phosphine methyl group shows that it must be *cis* rather than *trans* to the imido ligand.

Attempts to alkylate the nitride ligand in the complex $[ReNCl_2(PMe_2Ph)_3]$ with $Ph_3C^+BF_4^-$ or oxonium salts were not successful and only oily products resulted. However a blue crystalline material was obtained by reaction with $Ph_3C^+BF_4^-$ in dry acetone. The ^{1}H NMR spectrum was extremely complex in the region 1—4 ppm but the pattern characteristic of a *mer* arrangement of PMe_2Ph ligands could be discerned, and this was confirmed by the ^{31}P NMR spectrum. Integration indicated the presence of 9 or 10 protons in addition to those of the phosphines and the IR spectrum showed a band at 1720 cm^{-1} characteristic of a carbonyl group. This data coupled with elemental analysis for derivatives with different counter anions suggest the formulation $[Re(NCMe_2CH_2COMe)Cl_2(PMe_2Ph)_3]^+$. The imido substituent presumably arises from the condensation of two solvent molecules in the presence of the carbonium ion. Unfortunately, the crystals so far obtained have not been suitable for an X-ray crystal structure determination, and the precise formulation is not certain.

Attempts to deprotonate $[Re(NMe)(S_2CNMe_2)_2(PMe_2Ph)]BF_4$ to generate a methyleneimido derivative were not successful, and although a colour change occurred on treatment with base, only green oily compounds could be isolated. The activation of the coordinated imido ligands by electrochemical reduction will be the subject of a forthcoming paper.

TABLE 1

ORGANO-IMIDO COMPLEXES OF MOLYBDENUM AND RHENIUM

	Complex	Colour	Analysis [a] (%)			Conductivity [b]	^{1}H NMR data (ppm) [c]	
			C	H	N		Imido protons	Dithiocarbamato protons
I	$[Mo(NMe)(S_2CNEt_2)_3]BF_4$	Yellow	28.9 (29.3)	5.2 (5.0)	8.1 (8.5)	30	—	1.4m 3.8m
II	$[Mo(NMe)(S_2CNEt_2)_3]I$	Yellow-green	26.9 (27.5)	4.9 (4.9)	7.9 (8.0)	17	—	1.4m 3.8m
III	$[Mo(NEt)(S_2CNEt_2)_3]BPh_4$	Yellow	51.8 (51.2)	6.1 (5.8)	6.0 (5.8)	36	—	1.2m 3.65m
IV	$[Mo(NCPh_3)(S_2CNMe_2)_3]BF_4$	Yellow	40.3 (40.2)	4.6 (4.1)	6.3 (6.2)	28	7.2m	3.3 (1 : 2 : 1 : 2q)
V	$[Mo(NCPh_3)(S_2CNEt_2)_3]BF_4$	Yellow	45.5 (46.1)	5.4 (5.1)	6.3 (6.3)	30	7.2m	1.3m 3.7m
VI	$[Mo(NAr)(S_2CNEt_2)_3]Cl$ [e]	Orange	32.2 (32.4)	4.5 (4.3)	10.8 (10.8)	24	7.9m 7.2m	1.4m 3.9m
VII	$[Mo(NAr)(S_2CNEt_2)_3]PF_6$ [e]	Red	28.9 (28.4)	3.9 (3.7)	9.3 (9.5)	34	—	—
VIII	$[Re(NCPh_3)(S_2CNEt_2)_2]BF_4$	Pink	42.0 (42.1)	4.6 (4.2)	5.2 (5.1)	14	6.9—7.2m	1.20t, 3.54m
IX	$[Re(NCPh_3)(S_2CN(CH_2)_5)_2]BF_4$	Pink	39.1 (39.2)	4.0 (4.0)	4.8 (4.8)	17	7.1—7.4m	1.8m, 3.9m

X	$[Re(NCPh_3)(S_2CNMe_2)_2(PMe_2Ph)]BF_4$	Blue	43.0 (43.6)	4.4 (4.3)	4.7 (4.6)	29	7.0—7.4m	2.97s, 3.02s, 3.60s, 3.68s
XI	$[Re(NMe)(S_2CNMe_2)_2(PMe_2Ph)]BF_4$	Purple	26.4 (25.8)	3.9 (3.7)	6.0 (6.0)	31	1.77d [d]	3.11s, 3.23s, 3.49s, 3.51s
XII	$[Re(NSAr)Cl(S_2CNEt_2)_2]$ [e]	Yellow	26.7 (26.3)	3.3 (3.1)	9.4 (9.6)	2.8	8.0—9.0m	1.4m 3.8m
XIII	$[Mo(NSAr)(S_2CNMe_2)_3]Cl$ [e]	Yellow	25.8 (25.4)	3.0 (2.6)	10.0 (10.5)	3.2	8.5—9.0m	3.4m
XIV	$[Mo(BSAr)(S_2CNEt_2)_3]Cl$ [e]	Yellow	30.6 (31.1)	3.9 (4.1)	10.2 (10.4)	1.0	—	—
XV	$[Mo(NSAr)(S_2CNEt_2)_3]PF_6$ [e]	Orange	28.1 (28.1)	3.7 (3.7)	9.2 (9.4)	28	8.2—9.1m	1.4m, 3.9m
XVI	$[Mo(NSO_2Ph)(S_2CNEt_2)_3]Cl$	Yellow	33.9 (34.5)	5.0 (4.8)	7.5 (7.7)	1.9	—	—
XVII	$[Mo(NSO_2Ph)(S_2CNEt_2)_3]PF_6$	Red-orange	30.9 (30.8)	4.7 (4.3)	6.2 (6.8)	35	7.6—7.9m	1.3m, 3.8m
XVIII	$[Mo(NSO_2Ph)(S_2CNMe_2)_3]PF_6$	Red	23.6 (23.8)	3.3 (3.0)	6.8 (7.4)	32	7.6—8.0m	3.4m
XIX	$[Mo(NCOPh)(S_2CNEt_2)_3]PF_6$	Orange	32.7 (32.8)	4.6 (4.4)	6.9 (7.0)		7.4—8.0m	1.4m, 3.9m

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[a] Calculated values in parenthesis. [b] In mho cm^2 mol^{-1}, measured in $C_2H_4Cl_2$ solution. [c] Measured in $CDCl_3$ or CD_2Cl_2 solution. [d] $|^4J(HCNReP)| = 3.8$ Hz. [e] Ar = 2,4-$(O_2N)_2C_6H_3$.

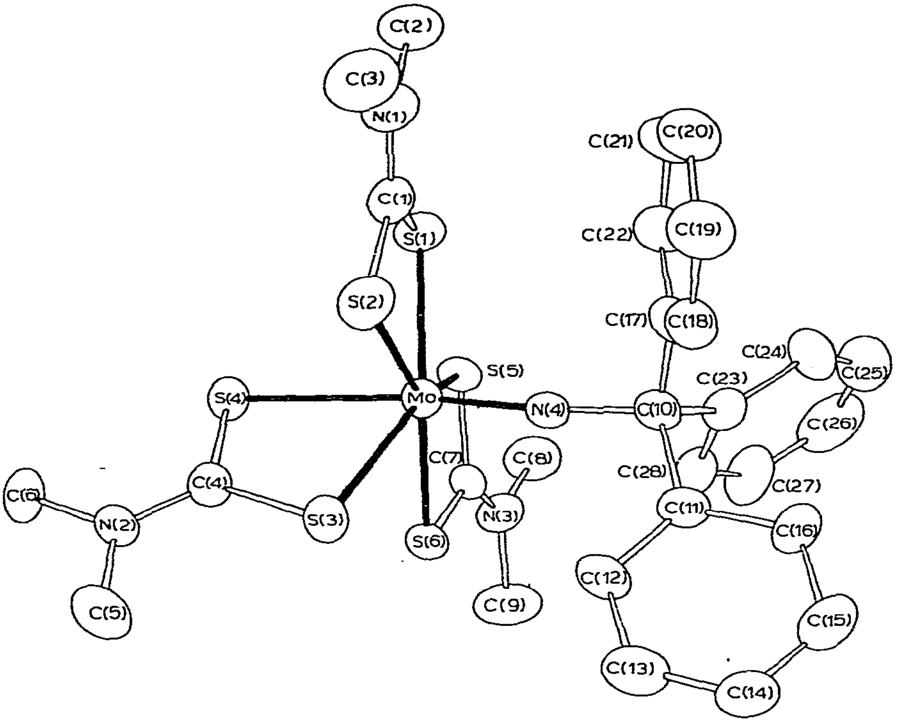

Fig. 1. ORTEP representation of the cation $[Mo(NCPh_3)(S_2CNMe_2)_3]^+$.

Imido complexes to date have been confined to alkyl, halogenated alkyl, aroyl and aryl groups. We therefore decided to determine the structures of the complexes $[Mo(NCPh_3)(S_2CNMe_2)_3]^+$ and $[Mo(NSO_2Ph)(S_2CNMe_2)_3]^+$ to examine the effect of these novel substituents on the geometry of the imido group. No triphenylmethyl or benzene sulphoxylimido derivatives have previously been reported, although a $Cu{=}NSO_2Ph$ intermediate was postulated in the copper-catalysed decomposition of benzenesulphonylazide [5].

X-ray crystal structure determinations

Details of the crystal data and experimental conditions are collected in Table 2. ORTEP representations of the two structures are given in Figs. 1 and 2, and selected bond lengths and angles are collected in Tables 3 and 4. Tables of atomic positional and thermal parameters appear in Tables 5 and 6. Calculated hydrogen atom positions, structure factor tables and complete bond lengths and angles are available as supplementary material from the authors (JRD).

$[Mo(NCPh_3)(S_2CNMe_2)_3]BF_4$ *(IV)*

The molybdenum is essentially pentagonal bipyramidally coordinated. The pentagonal plane is defined by atoms S(1), S(2), S(3), S(5) and S(6) and of these only S(3) deviates significantly from the least squares plane (see Table 7).

TABLE 2

CRYSTAL DATA AND EXPERIMENTAL DETAILS OF THE X-RAY DIFFRACTION STUDIES

	$[Mo(NCPh_3)(S_2CNMe_2)_3]BF_4 \cdot 0.7\ CH_2Cl_2$	$[Mo(NSO_2Ph)(S_2CNMe_2)_3]PF_6$
(A) Crystal parameters at 21°C [b]		
a (Å)	12.318(3)	25.332(6)
b (Å)	13.388(3)	8.287(4)
c (Å)	13.830(2)	27.824(6)
α (°)	112.53(1)	90.0
β (°)	105.43(1)	97.19(3)
γ (°)	100.62(2)	90.0
V (Å^3)	1921.3	5793.0
F(0,0,0)	875	3039
Crystal system	Triclinic	Monoclinic
Absences	none	hkl, $h + k = 2m$; $h0l$, $l = 2m$
Space group	$P\bar{1}$	$C2/c$
Z	2	8
P(calc) (g cm^{-3})	1.49	1.73
P(obs) [c] (g cm^{-3})	1.47(2)	1.76(2)
Mol. wt.	860.2	756.7
(B) Measurement of intensity data		
Crystal dimensions	0.21 X 0.21 X 0.35 mm	0.21 X 0.49 X 0.18
Instrument	Nonius CAD 4	Nicolet k3/m
Radiation	Mo, $K_{\bar{\alpha}}$, graphite monochromatized (λ, 0.71073 Å)	Mo, $K_{\bar{\alpha}}$, graphite monochromatized (λ, 0.71073 Å)
Scan technique	*w*	*w*
Scan range (°)	1.0	1.0
Scan rate (° min^{-1})	4.0	3.0to 15
max θ (°)	45.0	45.0
Background measurements	stationary crystal-stationary counter, 10 s at each end of the *w* scan range	
Standards [d]	3 reflections every 100 data reflections	
No. of reflections collected	4513	3743
(C) Treatment of intensity data		
Induction of F_0^2 and (F_0^2)	Corrected for background, attenuation and Lorentz-polarization in the usual manner	
μ (cm^{-1})	7.89	10.41
observed unique data	4513, with $F_0 > 2.58\sigma(F_0)$	1346 with $F_0 > 6.0\sigma(F_0)$
k_1	0.049	0.085
k_2	0.081	0.074

Both complexes were crystallised from dichloromethane/diethyl ether at 4°C.

[a] All calculations were performed on a Data General Nova 3 computer with 32K of 16-bit words using versions of the Nicolet SHELXTL interactive crystallographic software package as locally modified. [b] From a least squares fitting of the setting angles of 25 reflections. [c] Flotation. [d] In all cases showed only random, statistical fluctuations. [e] $k_1 = \Sigma||F_0| - |F_0||/\Sigma|F_0|$. [f] $k_2 = [\Sigma w(|F_0| - |F_0|)^2/\Sigma|F_0|^2]^{1/2}$, $w = {}^1/\sigma^2(F)$.

This deviation arises from the small bite angle of 69° for the dithiocarbamate ligand spanning the axial and equatorial positions; the bit angles of the two equatorial dithiocarbamates are 68.6 and 68.5°, very close to the 72° angles expected for the equatorial vertices of an ideal pentagonal bipyramid. The C—N and C—S bond lengths for the dithiocarbamate ligand lie within the range

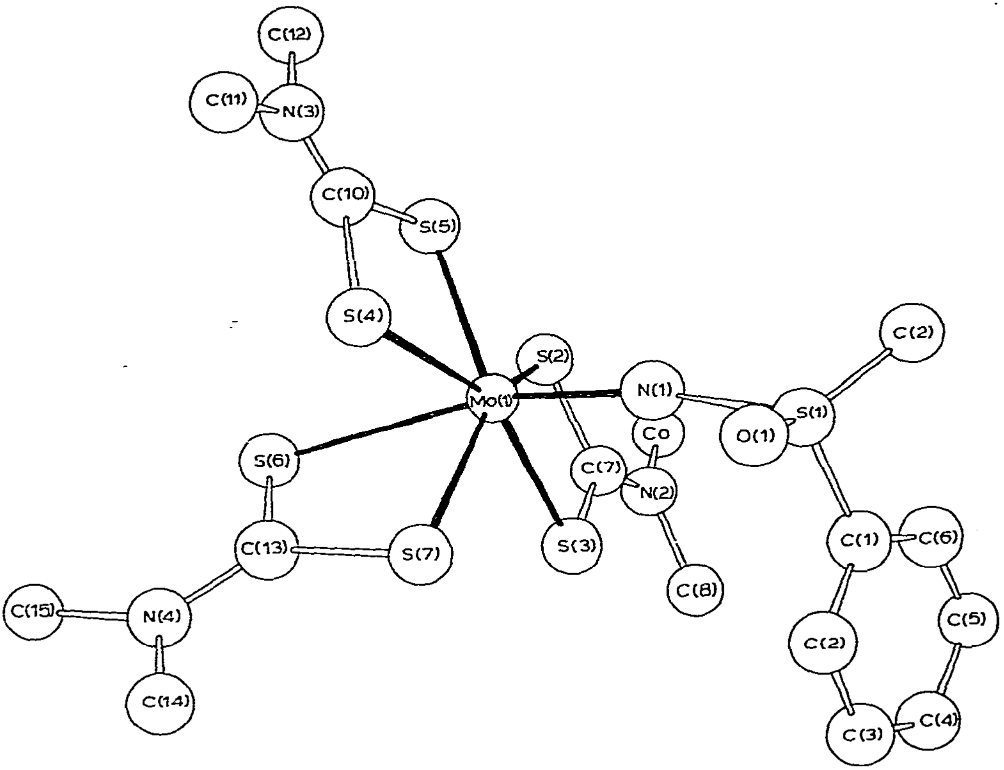

Fig. 2. ORTEP representation of the cation $[Mo(NSO_2Ph)(S_2CNMe_2)_3]^+$.

TABLE 3

IMPORTANT BOND LENGTHS AND ANGLES FOR $[Mo(NCPh_3)(S_2CNMe_2)_3] \cdot BF_4$

Mo—S(1)	2.491(2)	S(1)—Mo—S(2)	68.60(5)
Mo—S(2)	2.503(2)	S(2)—Mo—S(4)	83.69(6)
Mo—S(3)	2.504(2)	S(4)—Mo—S(3)	69.03(5)
Mo—S(4)	2.606(2)	S(3)—Mo—S(6)	74.52(5)
Mo—S(5)	2.485(1)	S(6)—Mo—S(5)	68.53(5)
Mo—S(6)	2.507(2)	S(5)—Mo—S(1)	70.92(5)
Mo—N(4)	1.731(2)	S(1)—Mo—S(4)	87.07(6)
N(4)—C(10)	1.455(8)	S(2)—Mo—S(4)	83.69(6)
C(1)—N(1)	1.306(10)	S(6)—Mo—S(4)	86.16(6)
C(1)—S(1)	1.717(5)	S(5)—Mo—S(4)	91.05(5)
C(1)—S(2)	1.709(7)	S(4)—Mo—N(4)	169.1(1)
C(4)—N(2)	1.307(8)	N(4)—Mo—S(1)	100.2(2)
C(4)—S(3)	1.734(7)	N(4)—Mo—S(2)	91.4(1)
C(4)—S(4)	1.700(6)	N(4)—Mo—S(3)	100.4(1)
C(7)—N(3)	1.291(7)	N(4)—Mo—S(6)	93.5(2)
C(7)—S(5)	1.719(8)	N(4)—Mo—S(5)	98.9(1)
C(7)—S(6)	1.710(5)	Mo—N(4)—C(10)	175.1(5)
C(10)—C(17)	1.535(9)	N(4)—C(10)—C(17)	105.0(5)
C(10)—C(23)	1.526(6)	C(4)—C(10)—C(23)	106.4(5)
C(10)—C(11)	1.532(8)	N(4)—C(10)—C(11)	110.7(5)

TABLE 4

IMPORTANT BOND LENGTHS AND ANGLES FOR [Mo(NSO$_2$Ph)(S$_2$CNMe$_2$)$_3$]PF$_6$

Mo—S(2)	2.467(8)	S(2)—Mo—S(3)	69.4(2)
Mo—S(3)	2.471(8)	S(2)—Mo—S(4)	139.0(2)
Mo—S(4)	2.499(8)	S(2)—Mo—S(5)	71.1(2)
Mo—S(5)	2.466(6)	S(2)—Mo—S(6)	90.3(3)
Mo—S(6)	2.525(8)	S(2)—Mo—S(7)	140.0(3)
Mo—S(7)	2.493(7)	S(2)—Mo—N(1)	103.5(7)
Mo—N(1)	1.70(2)	S(3)—Mo—S(4)	148.6(3)
N(1)—S(1)	1.71(2)	S(3)—Mo—S(5)	140.6(3)
S(1)—O(1)	1.43(2)	S(3)—Mo—S(6)	83.8(3)
S(1)—O(2)	1.46(2)	S(3)—Mo—S(7)	74.2(3)
S(1)—C(1)	1.76(3)	S(3)—Mo—N(1)	89.7(6)
C(7)—N(2)	1.39(4)	S(4)—Mo—S(5)	68.6(2)
C(7)—S(2)	1.69(3)	S(4)—Mo—S(6)	83.0(3)
C(7)—S(3)	1.71(3)	S(4)—Mo—S(7)	74.4(2)
C(10)—N(3)	1.27(3)	S(4)—Mo—N(1)	94.0(6)
C(10)—S(4)	1.71(2)	S(5)—Mo—S(6)	90.9(2)
C(10)—S(5)	1.76(3)	S(5)—Mo—S(7)	140.0(3)
C(13)—N(4)	1.32(3)	S(5)—Mo—N(1)	105.0(6)
C(13)—S(6)	1.71(2)	S(6)—Mo—S(7)	69.5(2)
C(13)—S(7)	1.67(2)	S(6)—Mo—N(1)	161.6(6)
		S(7)—Mo—N(1)	92.2(6)
		Mo—N(1)—S(1)	161.3(13)
		N(1)—S(1)—C(1)	100.3(11)
		N(1)—S(1)—O(1)	107.0(11)
		N(1)—S(1)—O(2)	107.0(11)
		O(1)—S(1)—C(1)	111.1(12)
		O(2)—S(1)—C(1)	106.0(14)

found for other molybdenum dithiocarbamate complexes.

The Mo—N(4) distance of 1.73 Å is very close to that found for other molybdenum imido complexes [6] and the Mo—N(4)—C(10) system is linear with an Mo—N(4)—C(10) angle of 175°. The imido ligand is axially distorted in the sense of being bent away from S(5) and S(2) and towards S(7) and S(3). The N(4)—C(10) distance of 1.46 Å indicates little multiple bonding between the imido nitrogen and the triphenylmethyl group. The phenyl rings of the latter are planar and are arranged in a propellor-like array to minimise steric repulsions.

Initial refinement of the methylene chloride solvent molecule produced chemically unreasonable bond lengths. After some experimentation to resolve the disorder, the methylene chloride atoms were fixed in positions producing a chemically reasonable model. A value of 0.7 for the population parameter was obtained from ^{1}H NMR data and was fixed. Subsequent refinement of the methylene chloride molecules was based only on thermal parameters.

[Mo(NSO$_2$Ph)(S$_2$CNMe$_2$)$_3$]PF$_6$(XVIII)

This complex is considerably more distorted from an idealised pentagonal bipyramidal geometry than the previous complex. The least squares plane through MoS(3)S(3)S(4)S(7) (Table 7) reveals the Mo lying some 0.3 Å above the plane together with S(3) and S(4), while S(7) lies well below it. The displacement of S(7) is attributable to the small bite angle of the axial-equatorial

(Continued on p. 121)

TABLE 5

POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS ($\times 10^2$) FOR [Mo(NCPh$_3$)(S$_2$CNMe$_2$)$_3$]BF$_4$·0.7 CH$_2$Cl$_2$ [a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.04599(4)	0.42273(4)	0.25316(3)	4.06(3)	5.24(4)	3.37(3)	1.97(2)	1.33(2)	1.78(2)
S(1)	0.0597(1)	0.3821(1)	0.4166(1)	6.32(9)	5.00(8)	3.98(8)	1.33(7)	1.80(7)	2.00(7)
S(2)	−0.0906(1)	0.2282(1)	0.1922(1)	5.86(9)	5.87(10)	4.78(9)	0.63(7)	1.27(7)	1.27(7)
S(3)	−0.1054(1)	0.3738(1)	0.0660(1)	4.89(9)	9.25(12)	3.67(8)	3.11(8)	1.42(7)	2.39(8)
S(4)	−0.1366(1)	0.4864(1)	0.2772(1)	4.99(9)	7.87(10)	4.25(8)	3.01(8)	1.96(7)	2.37(7)
S(5)	0.1836(1)	0.5949(1)	0.4297(1)	5.53(9)	5.12(8)	4.10(8)	1.49(7)	1.28(6)	2.10(7)
S(6)	0.1054(1)	0.5907(1)	0.2172(1)	5.56(9)	6.85(10)	5.13(9)	2.86(7)	1.93(7)	3.64(8)
N(1)	−0.0596(5)	0.1664(4)	0.3583(4)	7.85(35)	4.93(28)	7.32(34)	1.53(26)	3.73(29)	2.49(26)
N(2)	−0.2956(4)	0.4366(4)	0.0783(4)	4.70(27)	9.23(38)	5.59(30)	3.24(26)	1.88(23)	3.94(28)
N(3)	0.2862(4)	0.7646(4)	0.3951(4)	7.13(33)	5.49(31)	6.51(33)	1.59(27)	2.89(28)	3.06(27)
N(4)	0.1501(3)	0.3657(3)	0.2105(3)	4.30(24)	5.04(25)	3.25(22)	1.61(20)	0.99(19)	1.83(20)
C(1)	−0.0350(5)	0.2454(5)	0.3269(5)	4.94(32)	5.36(34)	5.19(33)	1.49(27)	2.13(27)	2.05(28)
C(2)	−0.0073(7)	0.1878(6)	0.4755(6)	9.52(51)	7.81(46)	7.61(46)	2.76(39)	3.90(40)	4.76(39)
C(3)	−0.1396(7)	0.0508(6)	0.2749(7)	9.24(54)	5.34(40)	10.74(59)	0.37(37)	3.66(46)	2.70(40)
C(4)	−0.1930(5)	0.4345(5)	0.1346(4)	4.24(29)	6.73(36)	4.57(31)	2.00(27)	1.70(25)	2.72(28)
C(5)	−0.3390(6)	0.3997(7)	−0.0428(6)	6.61(43)	14.28(69)	5.63(40)	3.79(44)	1.59(34)	5.04(45)
C(6)	−0.3715(5)	0.4815(6)	0.1362(6)	4.70(35)	11.04(56)	9.20(50)	3.82(37)	3.10(35)	5.30(45)
C(7)	0.2054(5)	0.6669(5)	0.3532(5)	5.51(33)	5.10(34)	5.10(32)	2.88(29)	2.49(27)	2.62(27)
C(8)	0.3710(6)	0.8209(6)	0.5131(6)	7.93(47)	6.78(43)	6.35(42)	0.11(36)	1.62(37)	1.89(35)
C(9)	0.3017(7)	0.8219(6)	0.3274(6)	10.77(58)	6.51(43)	9.07(52)	1.79(40)	3.64(46)	4.69(41)
C(10)	0.2352(4)	0.3110(4)	0.1783(4)	4.44(29)	5.14(31)	3.66(28)	2.23(25)	1.43(23)	1.77(24)

C(11)	0.2256(5)	0.2905(4)	0.0590(4)	4.92(31)	4.64(30)	4.01(29)	1.45(25)	1.51(25)	1.59(25)
C(12)	0.1389(6)	0.3076(6)	−0.0122(5)	7.77(42)	8.98(46)	4.62(34)	5.41(37)	2.68(32)	3.31(33)
C(13)	0.1338(7)	0.2864(6)	−0.1119(5)	10.09(54)	10.89(56)	5.37(39)	6.35(47)	4.51(38)	4.74(39)
C(14)	0.2171(6)	0.2499(5)	−0.1557(5)	9.29(49)	5.94(38)	4.82(36)	2.11(35)	3.10(36)	2.39(31)
C(15)	0.3037(6)	0.2329(6)	−0.0872(5)	7.07(42)	7.84(45)	6.02(41)	1.93(96)	3.81(36)	2.30(36)
C(16)	0.3101(5)	0.2538(5)	0.0203(5)	5.11(33)	7.88(42)	4.88(34)	2.69(11)	2.30(28)	2.47(31)
C(17)	0.2053(5)	0.2000(5)	0.1886(4)	4.94(31)	5.82(35)	4.59(31)	2.89(27)	1.91(26)	2.33(28)
C(18)	0.1568(5)	0.0953(5)	0.0975(5)	7.01(40)	6.06(38)	5.66(37)	2.67(32)	2.37(32)	2.94(32)
C(19)	0.1265(7)	−0.0033(6)	0.1097(7)	9.93(55)	6.15(42)	8.85(53)	2.70(39)	4.00(44)	3.20(39)
C(20)	0.1447(7)	0.0053(7)	0.2138(7)	9.98(56)	8.86(54)	9.93(60)	4.49(46)	4.10(48)	6.64(51)
C(21)	0.1906(7)	0.1086(7)	0.3057(6)	10.67(56)	9.74(57)	7.43(48)	5.70(48)	4.39(44)	5.83(47)
C(22)	0.2205(6)	0.2053(5)	0.2922(5)	8.26(45)	7.53(43)	5.17(36)	4.06(36)	2.95(33)	3.38(34)
C(23)	0.3586(5)	0.3952(5)	0.2955(4)	4.62(31)	6.41(38)	3.43(28)	2.23(27)	1.25(24)	1.78(26)
C(24)	0.4494(6)	0.3649(6)	0.3103(6)	5.81(31)	9.35(50)	6.81(43)	3.08(37)	0.84(35)	3.72(39)
C(25)	0.5616(6)	0.4456(9)	0.3792(7)	5.37(45)	14.31(81)	9.15(58)	3.10(51)	0.38(40)	6.46(60)
C(26)	0.5840(7)	0.5542(9)	0.3926(6)	6.01(48)	12.89(75)	4.69(40)	−0.15(49)	0.64(34)	1.07(45)
C(27)	0.4940(6)	0.5888(6)	0.3437(6)	6.16(44)	7.28(46)	8.01(48)	0.93(37)	3.03(39)	0.78(39)
C(28)	0.3826(5)	0.5087(5)	0.2763(5)	4.77(34)	6.33(40)	6.49(39)	1.87(30)	2.24(30)	1.75(32)
B	0.3225(8)	0.1105(9)	0.5941(8)	8.34(59)	11.59(72)	8.20(58)	4.22(54)	4.65(49)	5.44(55)
F(1)	0.3895(4)	0.1026(4)	0.5317(4)	10.31(32)	11.09(33)	9.71(31)	2.58(26)	6.15(27)	3.85(27)
F(2)	0.2253(6)	0.0108(6)	0.5326(7)	13.70(50)	16.58(58)	23.51(78)	0.98(43)	9.07(53)	10.54(57)
F(3)	0.2763(5)	0.1964(4)	0.6044(4)	12.68(40)	13.51(42)	12.69(40)	7.29(34)	6.34(34)	6.53(34)
F(4)	0.3821(8)	0.1215(9)	0.6930(6)	27.79(91)	44.24(134)	13.52(52)	26.53(100)	13.57(61)	19.14(73)
C(29) [b]	0.454	0.22	0.190	11.0(11)	27.1(23)	5.4(7)	2.1(13)	−0.1(7)	4.1(11)
Cl(1) [b]	0.566	0.126	0.192	22.2(5)	24.1(6)	12.9(4)	13.6(5)	8.0(4)	8.6(4)
Cl(2) [b]	0.384	−0.108	0.066	17.2(5)	23.1(7)	24.1(7)	4.8(5)	1.1(5)	11.2(6)

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[a] Estimated standard deviations in the least significant digits given are in parentheses. The thermal ellipsoid is of the form $\exp[-2\pi^2(a^{*2}U_{11} + b^{*2}U_{22} + c^{*2}U_{33} + 2a^*b^*U_{12} + 2a^*c^*U_{13} + 2b^*c^*U_{23})]$. [b] Population parameter fixed at 0.7.

TABLE 6

POSITIONAL AND THERMAL PARAMETERS (×10^2) FOR [Mo(NSO$_2$Ph)(S$_2$CNMe$_2$)$_3$]PF$_6$

Atom	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.02567(10)	0.68658(31)	0.10428(8)	3.5(2)	3.2(1)	2.7(1)	−0.1(1)	0.3(1)	3.2(1)
S(1)	−0.0706(3)	1.0027(8)	0.3264(3)	8.3(7)	3.6(6)	5.3(5)	1.4(5)	−1.1(5)	5.9(4)
S(2)	−0.0915(2)	0.6078(9)	0.4497(2)	3.9(5)	7.2(7)	4.1(4)	0.7(5)	0.2(4)	−1.7(5)
S(3)	−0.0990(3)	0.5306(9)	0.3507(2)	6.3(6)	4.3(6)	4.5(5)	−0.5(4)	−0.7(4)	−1.9(5)
S(4)	0.0683(3)	0.7845(9)	0.4019(2)	5.3(6)	5.9(7)	3.8(5)	−0.5(4)	0.5(4)	−3.4(5)
S(5)	0.0081(3)	0.7649(9)	0.4795(2)	4.7(5)	5.8(6)	3.0(4)	−1.6(4)	0.2(4)	−0.8(4)
S(6)	0.0185(3)	0.4139(9)	0.4077(2)	6.9(6)	4.8(6)	4.2(5)	1.7(4)	1.2(4)	0.4(5)
S(7)	0.0081(3)	0.5960(9)	0.3197(2)	6.2(6)	4.9(6)	2.7(4)	0.4(4)	0.2(4)	1.2(5)
P(1)	0.2221(4)	0.4295(13)	0.4056(4)	7.0(7)	7.3(8)	8.4(8)	0.8(7)	1.0(6)	−0.4(6)
F(1)	0.196(1)	0.327(3)	0.4388(9)	14.9(33)	19.2(30)	17.2(22)	5.3(22)	8.5(22)	−9.7(26)
F(2)	0.217(1)	0.289(3)	0.3718(8)	21.2(29)	14.7(26)	19.3(25)	−11.2(21)	1.6(22)	−1.1(22)
F(3)	−0.3290(9)	0.987(3)	0.384(1)	6.5(17)	15.7(29)	20.9(44)	0.9(30)	−7.1(23)	4.3(18)
F(4)	0.251(1)	0.538(3)	0.3716(9)	17.5(28)	17.4(28)	24.5(30)	3.6(25)	13.9(26)	3.6(23)
F(5)	0.230(1)	0.577(3)	0.4414(9)	15.6(24)	16.8(27)	23.3(28)	−12.4(23)	4.7(21)	−7.5(21)
F(6)	0.276(1)	0.373(3)	0.425(1)	15.4(25)	6.9(21)	23.5(44)	0.9(24)	−16.1(30)	−0.3(19)
O(1)	−0.0255(8)	1.035(2)	0.3017(6)	8.3(17)	13.0(22)	5.3(13)	4.5(14)	−0.3(12)	−5.4(16)
O(2)	−0.0985(9)	1.128(2)	0.3501(8)	15.7(24)	7.9(14)	11.7(19)	−2.1(13)	−3.2(17)	3.4(15)
N(1)	−0.0516(7)	0.859(2)	0.3691(6)	2.8(14)	3.0(16)	3.0(16)	4.4(13)	−2.3(10)	−2.5(11)
N(2)	−0.1812(9)	0.473(3)	0.4061(8)	7.3(20)	5.4(20)	6.4(17)	−0.2(15)	−1.7(16)	−1.8(16)
N(3)	0.1075(8)	0.888(3)	0.4903(7)	5.9(18)	6.9(20)	3.7(14)	−1.7(13)	0.8(13)	−3.1(16)
N(4)	0.0623(7)	0.326(3)	0.3297(7)	2.0(13)	5.9(17)	5.8(15)	0.5(15)	1.9(11)	−0.2(15)
C(1)	−0.120(1)	0.896(3)	0.2890(9)	4.4(8)					
C(2)	−0.104(1)	0.833(3)	0.2474(9)	5.6(8)					
C(3)	−0.146(1)	0.746(4)	0.2186(9)	6.7(10)					
C(4)	−0.194(1)	0.728(3)	0.2312(9)	8.0(11)					
C(5)	−0.209(1)	0.802(4)	0.273(1)	10.0(12)					
C(6)	−0.171(1)	0.881(3)	0.299(1)	7.0(10)					
C(7)	−0.130(1)	0.529(3)	0.4015(9)	4.9(8)					
C(8)	−0.211(1)	0.421(4)	0.3626(9)	10.0(13)					
C(9)	−0.204(1)	0.473(4)	0.4493(9)	7.7(11)					
C(10)	0.069(1)	0.826(4)	0.4624(8)	5.0(8)					
C(11)	0.155(1)	0.943(4)	0.4709(9)	7.6(11)					
C(12)	0.104(1)	0.906(3)	0.5402(7)	4.9(8)					
C(13)	0.0337(9)	0.434(3)	0.3495(8)	2.8(7)					
C(14)	0.078(1)	0.341(4)	0.2817(8)	6.7(10)					
C(15)	0.086(1)	0.179(3)	0.3574(9)	6.9(9)					

TABLE 7

DEVIATIONS OF ATOMS FROM SELECTED LEAST-SQUARES PLANES

$[Mo(NCPh_3)(S_2CNMe_2)_3]BF_4$		$[Mo(NSO_2Ph)(S_2CNMe_2)_3]BF_4$	
S(1)	−0.04	S(2)	−0.066
S(2)	0.02	S(3)	0.13
S(5)	0.04	S(4)	0.11
S(6)	−0.02	S(5)	−0.034
S(3)	−0.56	S(7)	−0.15
Mo	0.18	Mo	0.29
P	11.58	P	−0.36
Q	−6.13	Q	0.88
R	−3.84	R	−0.30
S	−3.21	S	2.18

Deviations are in Å. P, Q, R, and S are the variables for the normal equation of a plane $PX + QY + RZ = S$, in direct space.

dithiocarbamate and this also induces a bending of the Mo—S(6) vector towards S(7) away from a normal to the pentagonal plane. The imido nitrogen is bent away from S(2) (S(2)—Mo—N(1) = 104°) and S(5) (S(5)—Mo—N(1) = 105°). The nett result of these is considerable overall axial distortion with S(6)—Mo—N(1) = 162°.

These distortions do not appear to be steric in origin as there is no indication of steric interactions between the SO_2Ph group and the dithiocarbamate ligands. The S(1)—N(1) bond length of 1.71 Å indicates minimal π-bonding between sulphonyl sulphur and imido nitrogen. This suggests that the distortions are electronic in origin and result from the SO_2Ph group removing electron density from imido nitrogen and metal via the σ-bonding framework of the imido ligand. The Mo—N(1) distance is again similar to other molybdenum imido species, although in this instance there is considerable distortion from linearity with an Mo—N(1)—S(1) angle of 16°. The sulphoxyl oxygens are bent away both from N, and the dithiocarbamate ligand C(1)C(12)N(3)C(10)S(4)-S(5). It appears that although the metal—nitrogen bond distance is relatively insensitive to the nature of the imido substituent, the geometry about the imido nitrogen is more sensitive to the electronic distribution within the imido ligand.

Table 8 summarises X-ray structural data for a number of derivatives of the

TABLE 8

COMPARISONS OF SYSTEMS WITH MOLYBDENUM—NITROGEN MULTIPLE BONDS

Complex	M—N (Å)	M—N—X (°)	M—S_{trans} (Å)	M—S_{cis} (Å)	reference
$[MoN(S_2CNMe_2)_3]$	1.64	—	2.85	2.52(av)	3
$[Mo(NCPh_3)(S_2CNMe_2)_3]BF_4$	1.73	175	2.61	2.49—2.50	This work
$[Mo(NSO_2Ph)(S_2CNMe_2)_3]PF_6$	1.71	162	2.52	2.46—2.50	This work
$[Mo(NNPh)(S_2CNMe_2)_3]$	1.78	172	2.60	2.48—2.53	9
$[Mo(NNEtPh)(S_2CNMe_2)_3]^+$	1.70	170	2.56	2.50(av)	10
$[Mo(NNCO_2Et)(S_2CNMe_2)_3]$	1.73	179	2.60	2.48—2.53	11

type $[Mo(NX)(S_2CNR_2)_3]$ (where X = Ph_3C^+, SO_2Ph^+, $NEtPh^+$, NPh, NCO_2Et). Attachment of a substituent to the nitride nitrogen lengthens the metal—nitrogen bond by 0.7—0.16 Å, but there is no obvious correlation between the bond lengths and the nature of the substituent group. In line with the observation that for imido complexes with a formal eighteen electron configuration the imido group exerts little or no *trans* influence [6], only in the nitride is there significant lengthening of the molybdenum—sulphur bond *trans* to the multiply bonded group. Extensive studies of platinum complexes showed that the *trans* influence operates either by electron release from ligand to metal via σ-bonds, or by dative π-bonding from metal to ligand [7]. Since the above structures suggest that there is little π-interaction of the imido substituent with the nitrogen, the predominant effect must be in the σ-bonding framework, reducing the σ-donation from nitride to metal responsible for its high *trans* influence.

Experimental

All reactions were carried out under dinitrogen, using dry solvents, freshly distilled under dinitrogen. Infrared spectra were recorded on Pye-Unicam SP 1200 and SP 2000 spectrophotometers (Nujol mulls 200—4000 cm^{-1}). Varian HA 100 and JEOL PS 100 instruments were used to obtain ^1H NMR spectra in $CDCl_3$ or CD_2Cl_2 with tetramethylsilane as internal reference. Microanalyses were performed by Mr. and Mrs. A. Olney at the University of Sussex. The electrophilic substrates were purchased commercially and used as supplied. The nitrides $[MoN(S_2CNR_2)_3]$ [12], $[ReNCl_2(PMe_2Ph)_3]$ [12] and $[ReN(S_2CNR_2)_2]$ (R = Me_2, Et_2) [13] were prepared by literature methods. Roman numerals refer to Table 1.

Tris(diethyldithiocarbamato)methylimidomolybdenum tetrafluoroborate(I)

$[MoN(S_2CNEt_2)_3]$ (0.3 g) and $[Me_3O]BF_4$ (0.2 g) in dry dichloromethane (35 ml) were stirred at room temperature for 1 h. The solvent was then removed in vacuo and the oily yellow residue recrystallised as yellow needles from 1,2-dichloroethane/diethyl ether (0.2 g, 56%).

The other molybdenum imido complexes were synthesised in analogous fashion using solvents and reagents summarised below.

$[Mo(NMe)(S_2CNMe_2)_3]I$ (II). $[MoN(S_2CNMe_2)_3]$ + MeI in CH_2Cl_2.

$[Mo(NEt)(S_2CNEt_2)_3]BPh_4$ (III). $[MoN(S_2CNEt_2)_3]$ + $[Et_3O]BF_4$ in CH_2Cl_2. Change to MeOH and $NaBPh_4$.

$[Mo(NCPh_3)(S_2CNMe_2)_3]BF_4$ (IV). $[MoN(S_2CNMe_2)_3]$ + $[Ph_3C]BF_4$ in CH_2Cl_2.

$[Mo(NCPh_3)(S_2CNEt_2)_3]BF_4$ (V). $[MoN(S_2CNEt_2)_3]$ + $[Ph_3C]BF_4$ in CH_2Cl_2.

$[Mo(NAr)(S_2CNEt_2)_3]Cl$ (VI). $[MoN(S_2CNEt_2)_3]$ + ArCl in CH_2Cl_2.

$[Mo(NAr)(S_2CNEt_2)_3]PF_6$ (VII). VI + NH_4PF_6 in MeOH.

$[Mo(NSAr)(S_2CNMe_2)_3]Cl$ (XIII). $[MoN(S_2CNMe_2)_3]$ + ArSCl in CH_2Cl_2.

$[Mo(NSAr)(S_2CNEt_2)_3]Cl$ (XIV). $[MoN(S_2CNEt_2)_3]$ + ArSCl in CH_2Cl_2.

$[Mo(NSAr)(S_2CNEt_2)_3]PF_6$ (XV). XIV + NH_4PF_6 in MeCN.

$[Mo(NSO_2Ph)(S_2CNEt_2)_3]Cl$ (XVI). $[MoN(S_2CNEt_2)_3]$ + PhSOCl in CH_2Cl_2.

$[Mo(NSO_2Ph)(S_2CNEt_2)_3]PF_6$ (XVII). XVI + NH_4PF_6 in MeCN.

[Mo(NSO$_2$Ph)(S$_2$CNMe$_2$)$_3$]PF$_6$ (XVIII). [MoN(S$_2$CNMe$_2$)$_3$] + NH$_4$PF$_6$ + PhSO$_2$Cl in MeCN.

[Mo(NCOPh)(S$_2$CNEt$_2$)$_3$]PF$_6$ (XIX). [MoN(S$_2$CNEt$_2$)$_3$] + PhCOCl in MeCN.

Rhenium complexes

The precursor rhenium nitrides not previously reported were prepared as follows:

Bis(dimethyldithiocarbamato)nitrido(dimethylphenylphosphine)rhenium. [ReNCl$_2$(PMe$_2$Ph)$_3$] (0.5 g) and sodium dimethyldithiocarbamate were heated under reflux in acetone (40 ml) for 1 h. The solvent was removed in vacuo and the yellow residue recrystallised from dichloromethane/diethylether as yellow-orange needles (Found C, 29.3; H, 4.1; N, 7.0; $C_{14}H_{23}N_3PS_4Re$ calcd. C, 29.1; H, 4.0; N, 7.3%).

Bis(diethyldithiocarbamato)nitrido(dimethylphenylphosphine)rhenium. This was prepared similarly from [ReNCl$_2$(PMe$_2$Ph)$_3$] and sodium diethyldithiocarbamate, and recrystallised as yellow plates from 1,2-dichloroethane/ether. Found: C, 34.5; H, 5.1; N, 6.6. $C_{18}H_{31}N_3PS_4Re$ calcd.: C, 34.1; H, 4.9; N, 6.6%.

Bis(dimethyldithiocarbamato)triphenylmethylimidorhenium tetrafluoroborate(VIII). [ReN(S$_2$CNEt$_2$)$_2$] (0.5 g) and triphenylmethyl tetrafluoroborate (0.4 g) were stirred in dichloromethane for 0.5 h. Removal of solvent gave a pink residue which was recrystallised as pink needles from dichloromethane/diethylether.

The following complexes were synthesised analogously using the solvents and reagents indicated.

[Re(NCPh$_3$)(S$_2$CN(CH$_2$)$_5$)$_2$]BF$_4$ (IX). [ReN(S$_2$CN(CH$_2$)$_5$)$_2$] + [Ph$_3$C]BF$_4$ in CH$_2$Cl$_2$.

[Re(NCPh$_3$)(S$_2$CNMe$_2$)$_2$(PMe$_2$Ph)]BF$_4$ (X). [ReN(S$_2$CNMe$_2$)$_2$(PMe$_2$Ph)] + [Ph$_3$C]BF$_4$ in CH$_2$Cl$_2$.

[Re(NMe)(S$_2$CNMe$_2$)$_2$(PMe$_2$Ph)]BF$_4$ (XI). [ReN(S$_2$CNMe$_2$)$_2$(PMe$_2$Ph)] + [Me$_3$O]BF$_4$ in CH$_2$Cl$_2$.

[Re(NSAr)Cl(S$_2$CNEt$_2$)$_2$] (XII). [ReN(S$_2$CNEt$_2$)$_2$] + ArSCl in warm MeCN.

Reaction of [ReNCl$_2$(PMe$_2$Ph)$_3$] with [Ph$_3$C]BF$_4$ in acetone

[ReNCl$_2$(PMe$_2$Ph)$_3$] (0.4 g) and [Ph$_3$C]BF$_4$ (0.2 g) were stirred in dry acetone (40 ml) for 2 h. The solvent was removed in vacuo and the residue recrystallised from 1,2-dichloroethane/diethylether as blue needles. (Found: C, 41.7; H, 4.9; N, 1.7; Cl, 8.3. $C_{30}H_{43}NBCl_2F_4OP_3$ calcd.: C, 41.4; H, 5.0; N, 1.6; Cl, 8.2%). The PF_6^- salt was prepared by anion exchange and recrystallised as blue needles (Found: C, 39.3; H, 4.9; N, 1.8 $C_{30}H_{43}NCl_2F_6OP_4$ calcd.: C, 38.8; H, 4.6; N, 1.5%).

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