The Reactions of Molybdenum Oxo-complexes with Substituted Hydrazines. Part 5.† The Preparation of Some Organodiazenido-complexes of Molybdenum

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We describe a series of complexes $[Mo(N_2Q)(S_2CNMe_2)_3]$ (Q = alkyl, aryl, or alkoxycarbonyl) and $[Mo(N_2Q)_2(S_2CNMe_2)_2]$ prepared from $[MoO_2(S_2CNMe_2)_2]$ and the appropriate hydrazine. Representative members of the former class of compounds can be protonated, alkylated, and arylated at the diazenido-nitrogen remote from the metal. The latter compounds are formed *via* intermediates which are probably $[Mo(N_2H_2Q)(N_2Q)(S_2CNMe_2)_2]$. The electrochemical properties of the new complexes are discussed.

THE organodiazenido-grouping, $-N_2R$, has been considered as helpful in understanding the chemistry of both N_2 and NO.[1] In fact, its chemistry, especially the structure, protonation, and reduction, is sufficiently interesting and unusual on its own account without having to justify real or imagined parallels to support its study. Nevertheless, our study has as its basis the parallel between organodiazenido-complexes and those of the diazenide ion, $HN{=}N^-$, which we consider to be the first reduction products of ligating dinitrogen but which are not as accessible for study as the organo-derivatives. Organodiazenido-complexes can be synthesised by a variety of processes including the reactions of diazonium salts with a complex anion or neutral complex,[2,3] the insertion of diazonium salts into metal-hydrogen bonds followed by removal of the protons,[4,5] and oxidative additions of diazonium salts.[6-8] Further methods involve diazotisation of metal nitrosyl [9] and protonation [10] or alkylation [11] of co-ordinated dinitrogen. Finally, there is a group of syntheses from substituted hydrazones and a metal halide,[12] from $Me_3Si{-}N{=}N{-}R$ (R = aryl) and a metal halide,[13] diaryltriazenes and a metal halide,[5] and the insertion of trimethylsilyldiazomethane into a molybdenum–hydrogen or tungsten–hydrogen bond.[14]

We report here a series of mono- and bis-(organodiazenido)-complexes of molybdenum, of types $[Mo(N_2R)(dtc)_3]$ and $[Mo(N_2R)_2(dtc)_2]$, prepared from $[MoO_2(dtc)_2]$ (dtc = diorganodithiocarbamate) and an appropriate hydrazine, together with observations concerning their structures, modes of formation, and reactivities with both electrophiles and nucleophiles.

RESULTS AND DISCUSSION

Mono(organodiazenido)-complexes.—(*a*) *Preparation*. The complexes $[Mo(N_2R)(dtc)_3]$ (see Table 1) are prepared by the reaction of the appropriate hydrazine, $RNHNH_2$ (*ca.* 2 equivalents), with $[MoO_2(dtc)_2]$ in dry refluxing methanol in the presence of 1 equivalent of Na[dtc]. The compounds discussed here are those for which R = alkyl, aryl, or carboxycarbonyl. Those with R = acyl or aroyl will be described elsewhere because their chemistry is very different and is still being developed.[15] In the absence of Na[dtc], yields are of the order of 40%, but reach 70—80% in its presence.

We do not yet understand in detail how the diazenido-complexes are formed. The simple condensation to yield a species $Mo{=}N{-}NHR$ is plausible, but evidently some internal redox step perhaps involving Mo–OH is necessary to remove the remaining hydrogen.

(*b*) *Structure and properties*. The complexes are all monomeric, diamagnetic, air-stable, crystalline solids. An *X*-ray structure analysis [16] of $[Mo(N_2Ph)(S_2CNMe_2)_3]$ shows it to be seven-co-ordinate, with a pentagonal-bipyramidal structure (Figure 1). It is likely that the majority of the complexes $[Mo(N_2R)(dtc)_3]$ have analogous structures. The plane of the phenyl carbons is bent away from the plane containing the Mo–N–N–C system by *ca.* 5°, indicating that through-conjugation from C_6H_5 to Mo is not maximised. If the 18-electron rule is obeyed by the complexes the N_2R group must be formulated as a three-electron donor, and this is consistent with its essentially linear MoNN chain.

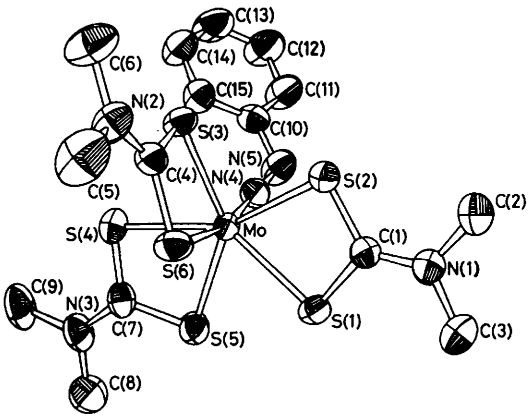

FIGURE 1 The molecular structure of $[Mo(N_2Ph)(S_2CNMe_2)_3]$

The ^{13}C n.m.r. spectra of the complexes as detailed in Table 2 show interesting features. This suggests that the chemical shifts, which may be assumed to be roughly proportional to the electron densities at the individual carbon atoms, are dependent upon X provided the carbon atoms form part of the diazenido-ligands, but that the chemical shifts of the carbons of the dtc ligands do not vary. This means that the effect of X cannot be making itself felt further than the molybdenum atom. The chemical shifts at, say, C^3 can be

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† Part 4, M. W. Bishop, J. Chatt, J. R. Dilworth, M. B. Hursthouse, and M. Motevalli, *J.C.S. Dalton*, 1979, 1603.

TABLE 1

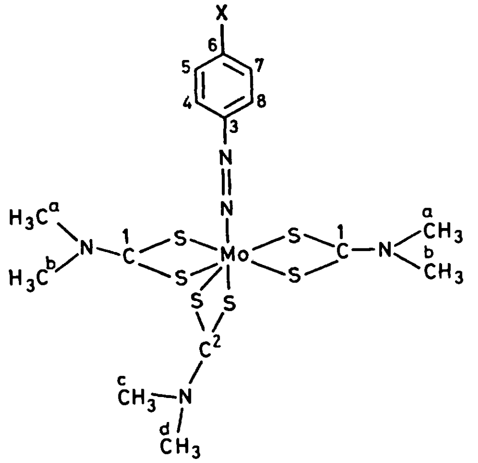
Mono- and bis-organodiazenido-complexes of molybdenum and some related complexes

	Colour	M.p.[a] (θ_c/°C)	M [b]	Region ν(NN) or ν(CN) (cm^{-1}) [c]	Analysis (%) [b]			
					C	H	N	X
(1) $[Mo(N_2Ph)(S_2CNMe_2)_3]$	Black	262—264	Insoluble	1 550br	32.4 (32.1)	4.2 (4.1)	12.6 (12.5)	34.2 (34.4) (S)
(2) $[Mo(N_2C_6H_4NO_2\text{-}p)(S_2CNMe_2)_3]$	Green-purple	248—250		1 545br	29.4 (29.7)	3.8 (3.6)	13.5 (13.7)	
(3) $[Mo(N_2C_6H_4NO_2\text{-}m)(S_2CNMe_2)_3]$	Brown	243 (decomp.)		1 505, 1 535br	30.0 (29.7)	2.7 (3.6)	13.8 (13.7)	
(4) $[Mo(N_2C_6H_4NO_2\text{-}o)(S_2CNMe_2)_3]$	Red-brown	133		1 505	29.6 (29.7)	3.7 (3.6)	13.8 (13.7)	
(5) $[Mo(N_2C_6H_4Cl\text{-}p)(S_2CNMe_2)_3]$	Black	256—258	643 (596)	1 545	29.9 (30.2)	3.7 (3.7)	11.5 (11.7)	6.9 (6.0) (Cl) 32.2 (32.0) (S)
(6) $[Mo(N_2C_6H_4Cl\text{-}m)(S_2CNMe_2)_3]$	Black-brown	234		1 515br	30.0 (30.2)	3.7 (3.7)	11.8 (11.7)	
(7) $[Mo(N_2C_6H_4Cl\text{-}o)(S_2CNMe_2)_3]$	Black	210 (decomp.)		1 515	30.1 (30.2)	4.0 (3.7)	11.6 (11.7)	
(8) $[Mo(N_2C_6H_4F\text{-}p)(S_2CNMe_2)_3]$	Black-brown	109		1 535br	31.1 (31.1)	4.0 (3.8)	11.7 (12.1)	
(9) $[Mo(N_2C_6H_4Me\text{-}p)(S_2CNMe_2)_3]$	Black	229		1 530	33.4 (33.4)	4.5 (4.4)	12.0 (12.2)	
(10) $[Mo(N_2C_6H_4Me\text{-}m)(S_2CNMe_2)_3]$	Black-brown	228		1 520br	33.4 (33.4)	4.4 (4.4)	12.0 (12.2)	
(11) $[Mo(N_2C_6H_4Me\text{-}o)(S_2CNMe_2)_3]$	Brown	250		1 515	33.5 (33.4)	4.4 (4.4)	12.1 (12.2)	
(12) $[Mo(N_2C_6H_4OMe\text{-}p)(S_2CNMe_2)_3]$	Black	258—260		1 550	31.7 (32.5)	4.2 (4.2)	11.4 (11.8)	
(13) $[Mo(N_2C_6H_4OMe\text{-}m)(S_2CNMe_2)_3]$	Black-brown	260		1 540	32.6 (32.5)	4.0 (4.2)	11.8 (11.8)	
(14) $[Mo(N_2C_6H_4OMe\text{-}o)(S_2CNMe_2)_3]$	Black-brown	>260		1 525br	32.6 (32.5)	3.9 (4.2)	11.7 (11.8)	
(15) $[Mo(N_2Me)(S_2CNMe_2)_3]$	Green	162—164	513 (499)	1 592, 1 540	24.2 (24.1)	4.4 (4.2)	13.9 (14.0)	
(16) $[Mo(N_2OCOBu^t)(S_2CNMe_2)_3]$	Orange	222		1 532, 1 515	28.6 (28.7)	4.9 (4.6)	11.8 (12.0)	
(17) $[Mo(N_2Ph)\{S_2CN(CH_2)_5\}_3]$	Brown	252—254	722 (681)	1 530	42.5 (42.3)	5.4 (5.1)	10.4 (10.3)	28.5 (28.2) (S)
(18) $[Mo(N_2Me)\{S_2CN(CH_2)_5\}_3]$	Green	155—158		1 583, 1 510	35.7 (36.8)	5.5 (5.3)	11.0 (11.3)	
(19) $[Mo(N_2Me)(S_2CNEt_2)_3]$	Green-brown	152—153	560 (583)	1 570, 1 500	32.7 (33.0)	5.6 (5.6)	11.6 (12.0)	
(20) $[Mo(N_2C_6H_4OMe\text{-}p)(S_2CNMePh)_3]$	Brown	255—257		1 550, 1 480	47.3 (47.9)	4.1 (4.0)	8.9 (8.0)	
(21) $[Mo(N_2C_6H_4OMe\text{-}p)(S_2CNPh_2)_3]$	Black	244—246	973 (963)	1 540, 1 490	57.3 (57.3)	4.2 (3.8)	7.5 (7.3)	19.8 (19.9) (S)
(22) $[Mo(N_2Me)(S_2CNPh_2)_3]$	Brown	146—148	915 (871)	1 585, 1 490	54.7 (55.1)	4.0 (3.8)	6.7 (8.0)	
(23) $[Mo(N_2Ph)_2(S_2CNMe_2)_2]$	Purple	240		1 570 (m), 1 580 (m), 1 610 (m), 1 640 (m)	38.9 (39.6)	4.2 (4.0)	14.9 (15.4)	
(24) $[Mo(N_2C_6H_4Br\text{-}p)_2(S_2CNMe_2)_2]$	Purple	172		1 565 (w), 1 590 (m), 1 610 (w), 1 640 (m)	30.5 (30.7)	3.4 (2.9)	11.4 (11.9)	
(25) $[Mo(N_2C_6H_4OMe\text{-}p)_2(S_2CNMe_2)_2]$	Red	104		1 580 (m), 1 605 (m)	39.1 (39.6)	4.5 (4.3)	13.3 (13.9)	
(26) $[Mo(N_2Me)_2(S_2CNMe_2)_2]$	Orange-red	135		1 600 (s), 1 660 (s)	22.8 (22.8)	4.4 (4.3)	19.5 (19.9)	
(27) $[Mo(N_2Ph)_2\{S_2CN(CH_2)_5\}_2]$ [d]	Orange	205 (decomp.)		1 570 (m), 1 590 (m), 1 600 (m), 1 635 (m)				
(28) $[Mo(N_2Ph)_2(S_2CNEt_2)_2]$	Purple	103		1 565 (m), 1 595 (m), 1 600 (m), 1 635 (m)	44.0 (43.8)	5.0 (5.0)	14.2 (13.9)	
(29) $[Mo_2(N_2H_2Ph)(N_2Ph)(S_2CNMe_2)_2]$	Orange	172		1 540 (m), 1 630 (m)	38.6 (39.5)	4.7 (4.4)	14.8 (15.3)	
(30) $[Mo(N_2H_2Me)(N_2Me)(S_2CNMe_2)_2]$	Orange-red	144		1 600 (m), 1 650 (w)	22.7 (22.6)	4.6 (4.7)	19.1 (19.8)	
(31) $[Mo(N_2H_2COOPh)(N_2COOPh)(S_2CNMe_2)_2]$	Orange	173		1 665 (s, br)	38.6 (39.5)	4.7 (4.4)	14.8 (15.3)	
(32) $[Mo(N_2H_2COOEt)(N_2COOEt)(S_2CNMe_2)_2]$	Yellow	174		1 630 (s), 1 665 (w), 1 700 (s)	25.7 (24.9)	3.8 (4.2)	14.9 (14.5)	
(33) $[Mo(N_2H_2COOBu^t)(N_2COOBu^t)\text{-}(S_2CNMe_2)_2]$	Orange	138		1 635 (s), 1 650 (m), 1 690 (s)	32.3 (32.2)	5.4 (5.4)	14.1 (14.1)	

[a] Generally with decomposition. [b] Calculated values are given in parentheses. [c] Nujol mulls. [d] Sample identified by spectroscopic properties only.

TABLE 2

Carbon-13 n.m.r. chemical shifts for the complexes $[Mo(N_2C_6H_4X\text{-}p)(S_2CNMe_2)_3]$ in CD_2Cl_2 solution at *ca.* 30 °C in p.p.m. relative to tetramethylsilane



X	C^1	C^2	C^3	$C^{4(8)}$	$C^{5(7)}$	C^6	C^a	C^b	C^c	C^d
NO_2	−205.2	−200.2	−157.1	−119.8	−124.8	−142.5	−37.5	−38.3	−40.5	
Cl	−206.6	−200.0	−145.0	−128.4	−128.4	−128.1	−37.4	−38.3	−40.5	−40.8
F	−206.8	−200.1	−142.7	−121.6	−114.7	−115.6	−37.4	−38.2	−40.0	−40.7
H	−206.8	−200.1	−147.9	−128.4	−120.7	−123.6	−37.4	−38.2	−40.4	
Me	−205.0	−200.0	−143.9				−37.3	−38.2	−40.4	−40.7
OMe	−204.3	−199.8		−121.6	−125.4	−114.4	−37.6	−38.4	−40.5	

correlated roughly with either Hammett function σ_p or σ_p^+, and so the significance of such correlations is not clear. However, the oxidation potentials of the complexes correlate much more satisfactorily with the σ_p functions of X [17] than with σ_p^+, and the activation energies for methyl interchange of the dtc groups in the ^1H n.m.r. spectra also correlate with σ_p.[18] This also indicates [17,18] that both phenomena operate through inductive effects transmitted only as far as the molybdenum. In what is possibly a similar manifestation of this effect, the Ru($3p_{\frac{3}{2}}$) binding energies in $[RuCl_3(N_2C_6H_4X)(PPh_3)_2]$ are believed to vary linearly with σ for X.[19]

In contrast to this dependence on X the lowest-energy charge-transfer bands in the molybdenum complexes are all found at *ca.* 415 nm in solution in dichloromethane, independent of X, which is less easy to rationalise without a detailed analysis of the origin of these bands, which we have been unable to undertake.

The complexes show one or two bands in the region 1 480—1 600 cm^{-1} which are assignable to ν(N=N) of the diazenido- or ν(C=N) of the dithiocarbamato-ligands. The complexes $[MBr(N_2R)(Ph_2PCH_2CH_2PPh_2)_2]$ (M = Mo or W; R = alkyl) also show complex bands in this region which do not allow easy assignment.[11] The complexes (20) and (21) (see Table 1) have ν(C=N) at <1 500 cm^{-1}. The higher bands (at 1 550 and 1 540 cm^{-1}, respectively) disappear upon alkylation (see below) so that these higher bands are probably assignable to ν(N=N).

The monodiazenido-complexes can be oxidised by an excess of dibromine to give $[Mo(N_2R)(dtc)_3]^+$. The oxidation can be monitored electrochemically. Cyclic voltammetry suggests a one-electron reversible oxidation. The precise value of the redox potential depends critically on the inductive electron-releasing properties of the substituent X in $[Mo(N_2C_6H_4X)(dtc)_3]$, but is independent of mesomeric effects.[17] None of the complexes can be reduced in the potential range accessible to us.

The diazenido-ligand, when acting as a three-electron donor, should be susceptible to electrophilic attack at the nitrogen remote from the metal. Attack is not invariably observed, however, witness the difference in reactivity towards protons of $[ReCl_2(N_2Ph)(PMe_2Ph)_3]$ and $[ReCl_2(N_2Ph)(NH_3)(PMe_2Ph)]$. The former does not react with protons whereas the latter, with a similar diazenido-ligand, does.[12]

The complexes $[Mo(N_2R)(dtc)_3]$ react with acids, HX, both gaseous and aqueous, to yield the hydrazido(2—)-complexes $[Mo(N_2HR)(dtc)_3]X$ or $[Mo(N_2HR)(dtc)_3X]$, depending upon X. For X = Cl or Br, non-electrolytes of the latter type are produced (Table 3). For X = BF_4, electrolytes of the former class are formed. The proton can be removed by bases. This behaviour parallels very closely the reversible protonation of $[M(N_2H)(Ph_2PCH_2PPh_2)_2X]$ [10] and $[M(N_2R)(Ph_2PCH_2CH_2PPh_2)_2X]$ [11] (M = Mo or W; R = alkyl). Acylation and aroylation proceed normally for R = Me, but for R = Ph protonation by adventitious acid is observed.[15]

The i.r. spectra of these hydrazido(2—)-complexes are unexceptional. It was not possible to assign bands unequivocally to ν(NH), even after deuteriation, and although ν(N=H) must have disappeared in comparison to the diazenido-complexes the continued presence of ν(C=N) from the dithiocarbamates effectively masks this. Similarly N–*H* protons could not be detected in the ^1H n.m.r. spectra. This is again not unusual.

The complexes $[Mo(N_2R)(dtc)_3]$ also react with R′X [R′X = methyl iodide, benzyl bromide and, in one case,

TABLE 3

Products of the alkylation and protonation of molybdenum diazenido-complexes

	Colour	M.p.[a] (θ_c/°C)	M [b]	Conductivity/ ohm^{-1} cm^2 mol^{-1}	Analysis (%) [b]			
					C	H	N	X
(34) $[Mo(N_2MePh)(S_2CNMe_2)_3]I$	Yellow	212—214		34.5 [c]	27.5 (27.4)	3.8 (3.7)	9.8 (10.0)	
(35) $[Mo(N_2Me_2)(S_2CNMe_2)_3]I$	Yellow	189—191		Insol.[c]	20.4 (20.6)	4.0 (3.8)	10.5 (10.9)	
(36) $[Mo\{N_2Me(CH_2Ph)\}(S_2CNMe_2)_3]Br$	Yellow	193—195		37.4 [c]	29.7 (29.2)	4.2 (4.3)	10.1 (10.6)	
(37) $[Mo(N_2MePh)\{S_2CN(CH_2)_5\}_3]I$	Yellow	196—198		36.2 [c]	35.9 (36.5)	4.8 (4.6)	8.4 (8.5)	
(38) $[Mo(N_2EtPh)\{S_2CN(CH_2)_5\}_3][BF_4]$	Golden yellow	228—230		49.0 [c]	38.3 (38.3)	5.1 (5.2)	8.7 (8.6)	
(39) $[Mo\{N_2[C_6H_3(NO_2)_2\text{-}2,4]\}\{S_2CN(CH_2)_5\}_3]Cl$	Red-brown	144—146		32.1 [c]	35.9 (36.5)	4.4 (4.4)	12.3 (11.9)	
(40) $[MoCl(N_2MeH)(S_2CNMe_2)_3]\cdot CH_2Cl_2$	Yellow	>260		1.7 [d]	20.5 (21.2)	3.9 (3.9)	11.1 (11.3)	
(41) $[Mo(N_2MeH)(S_2CNMe_2)_3][BF_4]\cdot 2H_2O$	Yellow	220—223		38.2 [d]	20.5 (19.4)	3.9 (3.7)	11.0 (11.3)	
(42) $[MoCl(N_2PhH)(S_2CNMe_2)_3]$	Yellow-brown	248—250	531 (598)	2.0 [d]	30.5 (30.2)	3.8 (4.0)	12.0 (11.7)	
(43) $[MoCl(N_2PhH)\{S_2CN(CH_2)_5\}_3]\cdot CH_2Cl_2$	Red-brown	>260	663 (718)	2.0 [d]	37.4 (37.4)	5.1 (4.7)	14.0 (13.3)	
(44) $[MoBr(N_2PhH)\{S_2CN(CH_2)_5\}_3]\cdot H_2O$	Yellow-brown	154—156	719 (762)	1.9 [d]	36.8 (36.9)	5.0 (4.9)	8.7 (8.7)	14.0 (13.3) (Cl)
(45) $[Mo(N_2PhH)\{S_2CN(CH_2)_5\}_3][BF_4]\cdot 2H_2O$	Golden yellow	173—176	328 (787)	35.0 [d]	36.0 (35.8)	4.9 (5.0)	8.7 (8.7)	

[a] With decomposition. [b] Calculated values are given in parentheses. [c] In solution in CH_2Cl_2. [d] In solution in 1,2-dichloroethane.

even $2,4\text{-}(NO_2)_2C_6H_3Cl]$ to yield the dialkylhydrazido(2—)-complexes $[Mo(N_2RR')(dtc)_3]X$ (Table 3). The reaction with $[OEt_3][BF_4]$ gives an analogous product. Interestingly, although $[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ reacts with, for example, methyl bromide to give $[MoBr(N_2Me)(Ph_2PCH_2CH_2PPh_2)_2]$,[11] the latter methyldiazenido-complex shows no tendency to react further with methyl bromide.

The complexes $[Mo(N_2RR')(dtc)_3]^+$ form air-stable, diamagnetic, crystalline salts. The *X*-ray structure analysis[20] of $[Mo(N_2EtPh)\{S_2CN(CH_2)_5\}_3][BPh_4]$ confirms that alkylation takes place on the nitrogen remote from the metal. The ^1H n.m.r. spectra of the diorganohydrazido(2—)-complexes are as expected. That of $[Mo(N_2Me_2)(S_2CNMe_2)_3]I$ shows only one resonance (τ 6.48) assignable to both N-methyls of the hydrazido(2—)-ligand, confirming that alkylation takes place on the remote nitrogen. The ^1H n.m.r. spectrum of $[WBr(N_2Me_2)(Ph_2PCH_2CH_2PPh_2)_2]^+$ is similar in this respect.[11]

Bis(organodiazenido)-complexes.—(*a*) *Preparation.* If $[MoO_2(dtc)_2]$ is treated with an excess of the hydrazine hydrochloride (*ca.* 5 mol) and without the addition of any Na[dtc], then complexes $[Mo(N_2R)_2(dtc)_2]$ are formed. These are monomeric, diamagnetic, air-stable, crystalline solids (Table 1). In particular cases, and especially when the hydrazine is a carbazate, $ROCONHNH_2$, it is possible to isolate complexes which we formulate as $[Mo(N_2H_2CO_2R)(N_2CO_2R)(dtc)_2]$. These crystalline materials are stable in the solid state and in solution in the absence of air. Exposure of the solutions to air results in a clean conversion into $[Mo(N_2CO_2R)_2(dtc)_2]$. Thus the mixed hydrazido-diazenido-complexes are apparently intermediates in the formation of the bis(diazenido)-complexes.

(*b*) *Structure and properties.* If the 18-electron rule is obeyed, then both N_2R groups in $[Mo(N_2R)_2(dtc)_2]$ should have linear Mo–N–N systems, and N–N–C angles of *ca.* 120°. The ^1H n.m.r. spectrum of $[Mo(N_2Ph)_2(S_2CNMe_2)_2]$ shows that in solution in CD_2Cl_2 at 25 °C there are two distinct kinds of methyl groups each of which gives rise to a singlet (τ 6.64, 6.58). Substituted aryl compounds are similar (see Table 4). This is best accommodated on the basis of a *cis* structure (I). The ^{13}C n.m.r. spectra are also consistent with this [Table 5, which compares analogous mono- and bis-(diorganodiazenido)-complexes].

The possibility that the *cis*-diazenido-groups are linked to give some kind of tetrazene structure cannot be excluded. However, the mass spectrum of $[Mo(N_2Ph)_2(S_2CNMe_2)_2]$ shows ions with *m/e* corresponding to the parent mass *M*, $[M - (N_2Ph)]$, and $[M - (N_2Ph)_2]$, making it unlikely that the two N_2Ph groups are directly linked within the complex molecule. In the i.r. spectra

TABLE 4

The ^1H n.m.r. spectra (τ) of *cis*-$[Mo(N_2R)_2(dtc)_2]$ in CD_2Cl_2 at 28 °C

Complex	Diazenido-protons *	Dithio-carbamato-protons *
$[Mo(N_2Ph)_2(S_2CNMe_2)_2]$	2.52 (10, m)	6.58 (6, s); 6.64 (6, s)
$[Mo(N_2Ph)_2(S_2CNEt_2)_2]$	2.60 (10, m)	6.18 (8, m); 8.70 (12, m)
$[Mo(N_2Ph)_2\{S_2CN(CH_2)_5\}_2]$	2.50— 3.00 (10, m)	8.20— 8.60 (20, m)
$[Mo(C_6H_4Br\text{-}p)_2(S_2CNMe_2)_2]$	2.80 (8, q)	6.63 (6, s); 6.66 (6, s)
$[Mo(N_2C_6H_4OMe\text{-}p)_2(S_2CNMe_2)_2]$	2.80 (8, q); 6.18 (6, s)	6.54 (6, s); 6.60 (6, s)
$[Mo(N_2Me)_2(S_2CNMe_2)_2]$	6.36 (6, s)	6.56 (12, s)

* Relative intensities and multiplicities in parentheses; s = singlet, q = quartet, m = multiplet.

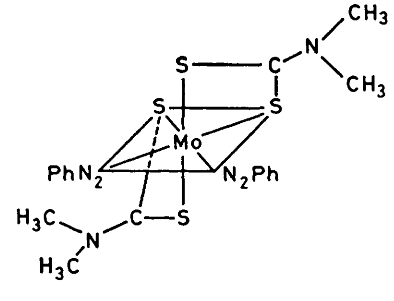
TABLE 5

The ^{13}C n.m.r. chemical shifts * of $[MoQ(S_2CNMe_2)_3]$ and $[MoQ_2(S_2CNMe_2)_2]$

	$[MoQ(S_2CNMe_2)_3]$		$[MoQ_2(S_2CNMe_2)_2]$		$Na[S_2CNMe_2]$
Q =	N_2Me	N_2Ph	N_2Me	N_2Ph	
Dithiocarbamato C	−200.0	−200.1 −206.8	−181.5	−205.0	−214.7
Dithiocarbamato-methyl C	−37.6 −38.4 −40.7	−37.4 −38.2 −40.4	−40.3 −40.1	−40.0	−44.8

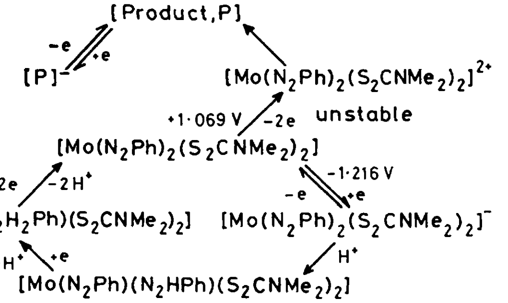
* In CD_2Cl_2 at 25 °C, relative to $SiMe_4$.

(see Table 1) there are strong bands at *ca.* 1 600 cm^{-1} the normal region for ν(NN) in singly bent diazenido-complexes. They are not nearly low enough to be considered characteristic of tetrazene-type ligands.



(I)

Electrochemically, the complexes of which *cis*-$[Mo(N_2Ph)_2(S_2CNMe_2)_2]$ is typical undergo an irreversible two-electron oxidation and a further reversible one-electron oxidation (see Scheme). The products of these oxidations have not been identified. The complexes can be reduced stepwise electrochemically, and generate the complexes which may be the materials $[Mo(N_2R)(N_2H_2R)(dtc)_2]$ considered in more detail below.



SCHEME Redox reactions of *cis*-$[Mo(N_2Ph)_2(S_2CNMe_2)_2]$ in dimethylformamide (dmf) solution–0.2 mol dm^{-3} $[NBu_4][BF_4]$; measured at Pt electrodes, 25 °C, potential scan rage 0.45 V s^{-1}, potentials with reference to s.c.e.

The complexes $[Mo(N_2R)_2(dtc)_2]$ also react with acids and other electrophiles, but the reactions are complex and have yet to be completely elucidated.

The Complexes $[Mo(N_2R)(N_2H_2R)(dtc)_2]$.—As discussed above, if the reaction of $[MoO_2(dtc)_2]$ with an organohydrazine hydrochloride in methanol is carried out with 5 mol equivalents of the hydrazine hydrochloride and without addition of Na[dtc], the bis(diazenido)-derivatives $[Mo(N_2R)_2(dtc)_2]$ can be isolated. In the particular cases of carbazates, phenylhydrazine, and methylhydrazine, when the reactions are carried out in the absence of air, intermediate complexes which analyse for $[Mo(N_2R)(N_2H_2R)(dtc)_2]$ can be isolated, as detailed in Tables 1 and 6. That they are indeed inter-

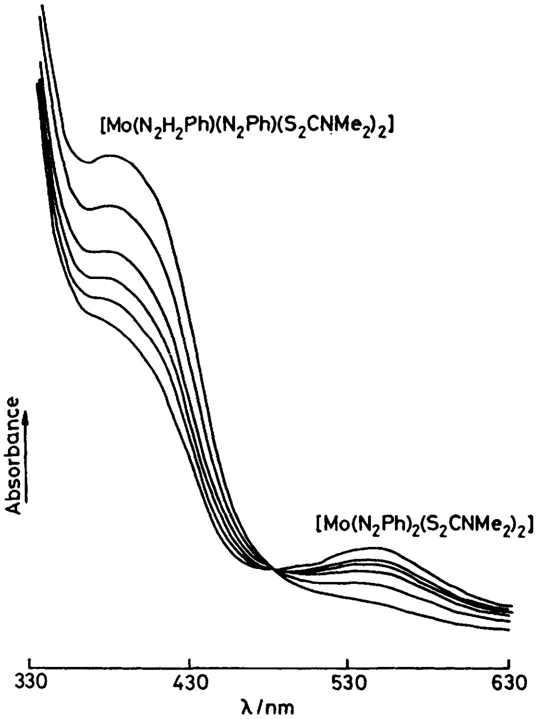


FIGURE 2 Isosbestic point in the conversion of $[Mo(N_2H_2Ph)(N_2Ph)(S_2CNMe_2)_2]$ into $[Mo(N_2Ph)_2(S_2CNMe_2)_2]$ in dichloromethane solution by aerial oxidation

TABLE 6

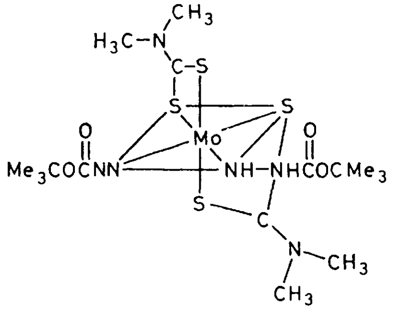
Spectral characteristics of *cis*-$[Mo(N_2H_2R)(N_2R)(dtc)_2]$

		Chemical shifts (τ) [b]	
Complex	ν(NH)/cm^{-1} [a]	N–*H*	Dithiocarbamato-C*H*$_3$
$[Mo(N_2H_2COOBu^t)(N_2COOBu^t)(S_2CNMe_2)_2]$	3 170w, 3 260w, 3 300w	2.88(1), 4.84(1)	6.56(3), 6.60(3), 6.62(3), 6.72(3)
$[Mo(N_2H_2COOEt)(N_2COOEt)(S_2CNMe_2)_2]$	3 170w, 3 270w	2.80(1)	6.61(3), 6.64(3), 6.66(3), 6.76(3)
$[Mo(N_2H_2Ph)(N_2Ph)(S_2CNMe_2)_2]$	3 140w, 3 260w, 3 370w	3.02(1)	6.56(3), 6.60(3), 6.66(3), 6.70(3)
$[Mo(N_2H_2Me)(N_2Me)(S_2CNMe_2)_2]$	3 100w, 3 200w		6.56(3), 6.59(3), 6.62(3), 6.64(3)

[a] Nujol mulls, w = weak. [b] Relative intensities in parentheses; all signals are singlets.

mediates in the formation of the bis(diazenido)-complexes is shown by the fact that exposure of solutions of the methyl and phenyl derivatives to air results in the formation of the bis(diazenido)-complexes without further compounds being involved (see Figure 2).

The formulation of these compounds as hydrazido-diazenido-complexes rests on the following spectroscopic data. The compounds all have a medium–strong band in the i.r. spectrum in the range 1 590—1 665 cm^{-1} assignable to ν(N=N), suggesting the presence of at least one diazenido-ligand (Tables 1 and 6). They also have bands at *ca.* 3 200 cm^{-1} assignable to N–H, but in only one case, [Mo(N$_2$COOBu^t)(N$_2$H$_2$COOBu^t)(S$_2$CNMe$_2$)$_2$], were two signals, suggesting two distinct kinds of N–H, observed in the ^{1}H n.m.r. spectrum. Both disappeared when D$_2$O was added to the test solution. The methyl groups of the dtc give rise to four distinct singlets suggesting four different methyl environments. A group of four signals in the ^{13}C n.m.r. spectrum is consistent with this and the carbonyl carbons are also resolved although both Bu^t methyl signals are apparently coincident.



(II)

These data are not unequivocal. However, we believe that they are best rationalised on the basis of structure (II), which we are attempting to confirm by *X*-ray structure analysis.

EXPERIMENTAL

Reactions were generally carried out under pure, dry dinitrogen in dry dioxygen-free solvents. Microanalyses (C, H, N, and halogen) were by Mr. A. G. Olney (University of Sussex) or Mr. P. E. Meadows (A.R.C. Unit of Nitrogen Fixation). Analyses for S were by Dr. A. Bernhardt. N.m.r. spectra were recorded by Mr. B. A. J. Alexander or Mr. P. E. Meadows using a JEOL PS-100 spectrometer (^{1}H) and by Mr. M. Siverns using a JEOL PFT-100 spectrometer (^{13}C). The internal standard was normally tetramethylsilane. Infrared spectra were generally obtained as Nujol mulls using Unicam SP 200 and 2000 machines. Melting points were determined with an Electrothermal Melting Point Apparatus, conductivities on a Portland Electronics Conductivity Bridge, and molecular weights with a Hitachi–Perkin-Elmer 115 Osmometer and solutions in 1,2-dichloroethane. Electrochemical measurements were made using Hi-Tek Instruments Potentiostat DT2101, a Chemical Electronics Waveform Generator RB1, and a Bryans X-Y recorder, 26000 A3.

Sodium salts of dithiocarbamates were prepared by cautiously adding carbon disulphide (1 : 1 equivalents) to the vigorously stirred aqueous solution of the appropriate amine (1 equivalent) and sodium hydroxide (1 equivalent). The crude dithiocarbamates were obtained as yellow to pink solids which were recrystallised from acetone as white plates.

Bis(dithiocarbamato)dioxomolybdenum complexes were prepared as exemplified below.

Bis(dimethyldithiocarbamato)dioxomolybdenum.[21]— To molybdenum trioxide (43.4 g, 0.301 mmol) was added butane-2,3-diol (250 cm^3). This mixture was heated under reflux for 15 min, the boiling stopped, and the hot mixture filtered in air. The colourless, viscous filtrate was seeded to yield white crystals of [MoO$_2${CH$_3$CH(O)CH(OH)CH$_3$}$_2$]·2CH$_3$CH(OH)CH(OH)CH$_3$ (A) (42.1 g, 32%).[22]

To a solution of (A) (11 g) in methanol (50 cm^3) was added a hot saturated solution of Na[S$_2$CNMe$_2$] (18 g) in methanol (50 cm^3) with vigorous stirring. The yellow precipitate was filtered, washed with methanol and Et$_2$O, and dried *in vacuo*. Yield 7—10 g. Addition of a 1 : 20 solution of concentrated nitric acid–water to the filtrate precipitated more material which was treated as above (Found: C, 19.8; H, 3.6; N, 7.3. C$_6$H$_{12}$MoN$_2$O$_2$S$_4$ requires C, 19.6; H, 3.3; N, 7.6%).

Organohydrazines were obtained commercially or synthesised by published methods. The diazenidotris(dithiocarbamato)-complexes were all prepared by the same basic method and only one example will be described in detail.

Tris(dimethyldithiocarbamato)(p-*nitrophenyldiazenido*)-*molybdenum*, (2).—To a mixture of [MoO$_2$(S$_2$CNMe$_2$)$_2$] (0.5 g, 1.36 mmol), Na[S$_2$CNMe$_2$] (0.36 g, 1.86 mmol), and *p*-NO$_2$C$_6$H$_4$NHNH$_2$ (0.70 g, 2.00 mmol) was added methanol (50 cm^3) and the resulting suspension heated under reflux for 0.75 h. The solvent was then removed at 10^{-3} mmHg * to yield a purple solid which was recrystallised from dichloromethane–methanol to yield purple *crystals*, green by reflected light (0.49 g, 60%).

The following derivatives of tris(dimethyldithiocarbamato)molybdenum were prepared in a similar fashion (yields in parentheses): *phenyldiazenido* (1) (73%); m-*nitrophenyldiazenido* (3) (32%); o-*nitrophenyldiazenido* (4) (29%); p-*chlorophenyldiazenido* (5) (21%); m-*chlorophenyldiazenido* (6) (21%); o-*chlorophenyldiazenido* (7) (24%); p-*fluorophenyldiazenido* (8) (19%); p-*tolyldiazenido* (9) (14%); m-*tolyldiazenido* (10) (28%); o-*tolyldiazenido* (11) (20%); p-*methoxyphenyldiazenido* (12) (20%); m-*methoxyphenyldiazenido* (13) (16%); o-*methoxyphenyldiazenido* (14) (31%); *methyldiazenido* (15) (78%); and *t-butoxycarbonyldiazenido* (16) (22%).

Using appropriate starting materials and the method outlined for (2), the following were also synthesised: *phenyldiazenidotris(piperidine*-N-*dithiocarboxylato)molybdenum*, (17) (72%); *methyldiazenidotris(piperidine*-N-*dithiocarboxylato)molybdenum* (18) (69%); *tris(diethyldithiocarbamato)methyldiazenidomolybdenum* (19) (62%); p-*methoxyphenyldiazenidotris(methylphenyldithiocarbamato)molybdenum* (20) (61%); *tris(diphenyldithiocarbamato)*-p-*methoxyphenyldiazenidomolybdenum* (21) (82%); and *tris(diphenyldithiocarbamato)methyldiazenidomolybdenum* (22) (71%).

Bis(dimethyldithiocarbamato)bis(phenyldiazenido)molybdenum (23).—To a mixture of [MoO$_2$(S$_2$CNMe$_2$)$_2$] (2.38 g, 6.47 mmol) and PhNHNH$_2$·HCl (4.67 g, 32.3 mmol), was added methanol (130 cm^3). The suspension was stirred in

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

air at 25 °C for 2 d. The bulk of the solvent was removed from the purple solution at 10^{-3} mmHg, and the concentrated solution held at −20 °C until purple *crystals* were formed. These were filtered off, washed with Et_2O, and dried *in vacuo*. Yield 0.75 g, 21%.

In a similar fashion the following bis(dimethyldithiocarbamato)-derivatives were prepared: *bis(p-bromophenyldiazenido)* (24) (22%); *bis(*p*-methoxyphenyldiazenido)* (25) (36%); and *bis(methyldiazenido)* (26) (63%). A similar method was used to prepare the following from appropriate starting materials: *bis(phenyldiazenido)bis(piperidine-*N*-dithiocarboxylato)molybdenum* (27) (31%), and *bis(diethyldithiocarbamato)bis(phenyldiazenido)molybdenum* (28) (23%).

*Bis(dimethyldithiocarbamato)(phenyldiazenido)(*N*-phenylhydrazido-*N′*)molybdenum* (29).—To $[MoO_2(S_2CNMe_2)_2]$ (4.67 g, 12.7 mmol) in methanol (250 cm³), was added $PhNHNH_2$ (6.85 g, 63.4 mmol) and the resulting suspension was stirred at 25 °C for 2 d. The orange precipitate was filtered off and washed with Et_2O to yield an orange *solid* (8.27 g, 76%) which was obtained as deep orange crystals from methanol.

The following bis(dimethyldithiocarbamato)molybdenum derivatives were prepared similarly: *methyldiazenido(methylhydrazido)* (30) crystallised from the preparative solution at −20 °C (29%); *phenoxycarbazato(phenoxycarbonyldiazenido)* (31) (76%); *ethoxycarbazato(ethoxycarbonyldiazenido)* (32), the initial precipitate in this case being $[Mo(N_2OCOEt_2)(S_2CNMe_2)_3]$ and the product was obtained from the filtrate at −20 °C (13%); *butoxycarbazato(butoxycarbonyldiazenido)* (33) (35%).*

Tris(dimethyldithiocarbamato)(ethoxycarbonyldiazenido)-molybdenum.—To a mixture of $[MoO_2(S_2CNMe_2)_2]$ (0.79 g, 2.15 mmol) and $EtOCONHNH_2$ (1.16 g, 11.2 mmol) was added methanol (50 cm³) and the resulting suspension stirred for 6 d. The suspension was then filtered and the filtrate worked up to give $[Mo(N_2OCOEt)(N_2H_2OCOEt)(S_2CNMe_2)_2]$ (see above). The precipitate was recrystallised from CH_2Cl_2–MeOH as orange *crystals*, m.p. 120—124 °C (decomp.), 0.23 g (19%) (Found: C, 25.7; H, 4.5; N, 13.8. $C_{12}H_{23}MoN_5O_2S_6$ requires C, 25.8; H, 4.9; N, 12.6%). The nature of this compound was confirmed by ¹H n.m.r. spectroscopy and *X*-ray structural analysis.[23]

*Tris(dimethyldithiocarbamato)[*N*-methyl-*N*-phenylhydrazido(2−)-*N′*]molybdenum Iodide* (34).—Methyl iodide (0.50 cm³) was added to (1) (0.40 g) in CH_2Cl_2 (30 cm³) and the mixture heated under reflux for 15 min. The solution was evaporated to *ca.* 5 cm³ at 10^{-2} mmHg and the *complex* precipitated as an orange-brown precipitate by addition of Et_2O (50 cm³). It was recrystallised from CH_2Cl_2–Et_2O as yellow needles (0.30 g, 60%).

In a similar fashion were prepared: *[*N*-methyl-*N*-phenylhydrazido(2−)-*N′*](piperidine-*N*-dithiocarboxylato)molybdenum iodide* (37), from (17) and MeI (68%); *tris(dimethyldithiocarbamato)[*N,N*-dimethylhydrazido(2−)-*N′*]molybdenum iodide* (35), from (25) and MeI (74%); *[*N*-benzyl-*N*-methylhydrazido(2−)-*N′*]tris(dimethyldithiocarbamato)molybdenum bromide* (36), from (14) and benzyl bromide (65%); *[*N*-ethyl-*N*-phenylhydrazido(2−)-*N′*](piperidine-*N*-dithiocarboxylato)molybdenum tetrafluoroborate* (38), from (17) and $[OEt_3][BF_4]$ (78%); and *[*N*-(2,4-dinitrophenyl)-*N*-methylhydrazido(2−)-*N′*](piperidine-*N*-dithiocarboxylato)molybdenum chloride* (39), from (17) and 1-chloro-2,4-dinitrobenzene, evaporating the mixture to dryness, extracting with CH_2ClCH_2Cl, and precipitating the product from the extract with Et_2O (66%).

*Chlorotris(dimethyldithiocarbamato)[*N*-methylhydrazido-(2−)-*N′*]molybdenum–Dichloromethane* (1/1) (40).—Hydrogen chloride was passed (30 s) into a solution of (15) (0.5 g) in CH_2Cl_2 (10 cm³). The warm solution was quickly filtered, and the *complex* crystallised as yellow needles as the solution cooled (0.41 g, 65%).

*Chloro[*N*-methylhydrazido(2−)-*N′*]tris(piperidine-*N*-dithiocarboxylato)molybdenum–Dichloromethane* (1/1) (43), was prepared analogously from (18).

*Tris(dimethyldithiocarbamato)[*N*-methylhydrazido(2−)-*N′*]molybdenum Tetrafluoroborate–Water* (1/2) (41).—Tetrafluoroboric acid (1 cm³) was added to a suspension of (15) (0.5 g) in methanol (20 cm³) and the red solution heated under reflux for 10 min. The solvent was removed at 10^{-3} mmHg and the yellow residue recrystallised from dmf–Et_2O as yellow *needles* (0.34 g, 55%). *[*N*-Phenylhydrazido(2−)-*N′*]tris(piperidine-*N*-dithiocarboxylato)molybdenum tetrafluoroborate–water* (1/2) (45), was prepared analogously from (17).

*Chlorotris(dimethyldithiocarbamato)[*N*-phenylhydrazido-(2−)-*N′*]molybdenum* (42).—Concentrated HCl (0.5 cm³) was added to (1) (0.4 g) suspended in methanol (20 cm³). The solution was heated under reflux for 15 min, and the solvent then removed at 10^{-3} mmHg. The residue was recrystallised from CH_2Cl_2–Et_2O as yellow-brown *needles* (0.28 g, 66%).

*Bromo[*N*-phenylhydrazido(2−)-*N′*]tris(piperidine-*N*-dithiocarboxylato)molybdenum–water* (1/2) (44), was prepared analogously from (17) and hydrobromic acid (61%).

[8/1396 *Received, 27th July, 1978*]

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* Recommended alternative names for the carbazato-ligands of complexes (31)—(33) are *N*-phenoxycarbonylhydrazido-*N′*, *N*-ethoxycarbonylhydrazido-*N′*, and *N*-butoxycarbonylhydrazido-*N′* respectively.

REFERENCES

[1] D. Sutton, *Chem. Soc. Rev.*, 1975, **4**, 443.

[2] M. B. Bisnette and R. B. King, *J. Amer. Chem. Soc.*, 1964, **86**, 5694.

[3] See, for example, W. E. Carroll, and F. J. Lalor, *J.C.S. Dalton*, 1973, 1754.

[4] G. W. Parshall, *J. Amer. Chem. Soc.*, 1965, **87**, 2133; 1967, **89**, 1822.

[5] K. R. Laing, S. D. Robinson, and M. R. Uttley, *J.C.S. Dalton*, 1973, 2713.

[6] S. Cenini, R. Ugo, and G. La Monica, *J. Chem. Soc.* (*A*), 1971, 3441.

[7] A. Gaughan, B. Haymore, J. A. Ibers, W. Meyers, T. Nappier, and D. Meek, *J. Amer. Chem. Soc.*, 1973, **95**, 6859.

[8] A. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1128.

[9] W. L. Bowden, W. F. Little, and T. J. Meyer, *J. Amer. Chem. Soc.*, 1973, **95**, 5084.

[10] J. Chatt, A. J. Pearman, and R. L. Richards, *J.C.S. Dalton*, 1976, 1520.

[11] J. Chatt, A. D. Diamantis, G. A. Heath, N. E. Hooper, and G. J. Leigh, *J.C.S. Dalton*, 1977, 688.

[12] P. G. Douglas, A. R. Galbraith, and B. L. Shaw, *Transition Metal Chem.*, 1975, **1**, 17.

[13] M. R. Churchill and K. G. Lin, *Inorg. Chem.*, 1975, **14**, 1133.

[14] M. F. Lappert and J. S. Poland, *Chem. Comm.*, 1969, 1061.

[15] M. W. Bishop, J. Chatt, and J. R. Dilworth, unpublished work.

[16] G. Butler, J. Chatt, G. J. Leigh, A. R. P. Smith, and G. Williams, *Inorg. Chim. Acta*, 1978, **28**, L165.

[17] G. Butler, J. Chatt, G. J. Leigh, and C. J. Pickett, *J.C.S. Dalton*, 1979, 113.

[18] E. O. Bishop, M. W. Bishop, J. Chatt, J. R. Dilworth, G. J. Leigh, and D. Orchard, *J.C.S. Dalton*, 1978, 1654.

[19] D. T. Clark, I. S. Woolsey, S. D. Robinson, K. R. Laing, and J. N. Wingfield, *Inorg. Chem.*, 1977, **16**, 1201.

[20] F. C. March, R. Mason, and K. M. Thomas, *J. Organometallic Chem.*, 1975, **96**, C43.

[21] F. W. Moore and M. L. Larson, *Inorg. Chem.*, 1967, **6**, 988; F. W. Moore and R. E. Rice, *ibid.*, 1968, **7**, 2510.

[22] R. J. Butcher, H. K. J. Powell, J. Wilkins, and S. M. Yong, *J.C.S. Dalton*, 1976, 356; R. J. Butcher, personal communication.

[23] G. Butler, J. Chatt, D. L. Hughes, W. Hussain, and G. J. Leigh, *Inorg. Chim. Acta*, 1978, **30**, L287.