Synthesis and Reactivity of the Paramagnetic Nitrosyl Complexes $[M(NO)(NCMe)_5]^{2+}$ (M = Cr or Mo), and the Crystal Structures of $[Cr(NO)(S_2CNEt_2)_3]$ and $[CrF(NO)(dppe)_2]$ †

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Excess of [NO]Y (Y = BF_4 or PF_6) and $[M(CO)_6]$ in acetonitrile afford paramagnetic $[M(NO)(NCMe)_5]Y_2$ (1; M = Cr or Mo) which reacts with NO gas (M = Mo) to give diamagnetic *cis*-$[Mo(NO)_2(NCMe)_4]Y_2$. At room temperature (1; M = Cr) and $[S_2CNR_2]^-$ yield $[Cr(NO)(S_2CNR_2)_3]$ (2; R = Me or Et) which affords *cis*-$[Cr(NO)_2(S_2CNR_2)_2]$ and $[Cr(S_2CNR_2)_3]$ in refluxing toluene; only *cis*-$[Cr(NO)_2\{S_2C_2(CN)_2\}_2]^{2-}$ is isolable from the reaction between (1; M = Cr) and $Na_2[S_2C_2(CN)_2]$. A crystal-structure determination of (2; R = Et) has revealed the geometry about chromium to be pentagonal bipyramidal with the nitrosyl ligand in an axial position; crystals are triclinic, space group $P\bar{1}$, with Z = 2, in a unit cell of dimensions a = 9.525(3), b = 9.903(5), c = 14.649(7) Å, α = 103.8(4), β = 74.5(3), and γ = 107.4(3)°. The structure has been solved from diffractometer data by the heavy-atom method, and refined to R = 0.040 for 3 033 observed reflections.

With 1,2-bis(diphenylphosphino)ethane (dppe) in acetonitrile (1; M = Cr or Mo) affords $[M(NO)(NCMe)(dppe)_2]Y_2$ (3; M = Cr) and $[M(NO)(NCMe)(dppe)_2]Y$ (4; M = Mo) which is oxidised to (3; M = Mo) by $[N_2C_6H_4F\text{-}p]Y$. Dppe and (1; M = Cr) also give $[CrX(NO)(dppe)_2]Y$ (5; X = F) which is reduced, as is (3; M = Cr), by $Na[BH_4]$ in tetrahydrofuran to $[CrX(NO)(dppe)_2]$ (6; X = F). The crystal structure of (6; X = F) has verified the *trans* disposition of the NO and F ligands; crystals are monoclinic, space group $P2_1/n$, with Z = 2, in a unit cell of dimensions a = 11.080(6), b = 16.352(6), c = 13.129(7) Å, and β = 109.17(4)°. The structure has been solved from diffractometer data by the heavy-atom method, and refined to R = 0.047 for 2 633 observed reflections.

Complexes (3) and (4) react with chloride ion to give $[MX(NO)(dppe)_2]Y$ (5; M = Cr or Mo, X = Cl) and $[MX(NO)(dppe)_2]$ (6; M = Mo, X = Cl) respectively, which are interconvertible by $[N_2C_6H_4F\text{-}p]Y$ oxidation [(6) to (5)] or $Na[BH_4]$ reduction [(5) to (6)]. The redox properties of complexes (1)—(6) have also been studied, by cyclic voltammetry, and the retention during electron transfer of the mutually *trans* disposition of the dppe ligands of (3)—(6) verified by ^{31}P n.m.r. and e.s.r. spectroscopy.

THE reactions of the nitrosonium ion, $[NO]^+$, with Lewis-base derivatives of the Group 6 metal carbonyls give either cationic nitrosyl complexes of the type $[M(CO)_3(NO)(L\text{-}L)]^+$ (M = Mo or W, L-L‡ = dppe,[1] dmpe, dcpe,[2] pdma,[3] phen, or bipy [4]), or products formed by one-electron oxidation, such as *trans*-$[Mo(CO)_2(dppe)_2]^+$ from [5] *cis*-$[Mo(CO)_2(dppe)_2]$. We now report that the parent hexacarbonyls, $[M(CO)_6]$ (M = Cr or Mo), react with [NO]Y salts (Y = BF_4 or PF_6) to give the paramagnetic dications $[M(NO)(NCMe)_5]Y_2$ (1; M = Cr or Mo) which undergo nitrile-substitution reactions with anionic and neutral ligands. The redox properties of complex (1) and of the substitution products have been studied by cyclic voltammetry, and structural assignment made *via* ^{31}P n.m.r. and e.s.r. spectroscopy. The structures of $[Cr(NO)(S_2CNEt_2)_3]$ and $[CrF(NO)(dppe)_2]$ have been determined by single-crystal *X*-ray diffraction studies.

RESULTS AND DISCUSSION

Synthetic Studies.—The addition of an excess of solid [NO]Y (Y = BF_4 or PF_6) to $[Cr(CO)_6]$ in acetonitrile results in vigorous gas evolution and the formation of a brown solution. Addition of diethyl ether affords quantitative yields of yellow paramagnetic $[M(NO)(NCMe)_5]Y_2$ (1; M = Cr) which has been characterised by i.r. spectroscopy and elemental analysis (Table 1). The e.s.r. spectrum (Table 2) of (1; M = Cr) in MeCN shows only one line, the lack of hyperfine coupling to the nitrosyl- and nitrile-nitrogen atoms contrasting with results found for analogous chromium(I) complexes [6] $[Cr(NO)L_5]^z$ (z = 2, L = NH_3 [7,8] or OH_2; [8] z = −3, L = CN [8] or CNS [9]).§

The isolation of high yields of (1; M = Mo) is not straightforward and relies on the efficient removal of NO gas ¶ from the reaction. Thus, under a blanket of nitrogen, $[Mo(CO)_6]$ and $[NO][PF_6]$ in acetonitrile afford *cis*-$[Mo(NO)_2(NCMe)_4][PF_6]_2$,[11] but passage of a vigorous stream of nitrogen gas *through* the reaction mixture gives (1; M = Mo). That (1; M = Mo) readily reacts with NO is demonstrated by slowly adding a solution of the gas in MeCN to the yellow mononitrosyl in the same solvent; the green dinitrosyl is immediately formed. By contrast (1; M = Cr) does not react even when gaseous NO is passed directly through a solution of the complex in MeCN.

Complex (1; M = Mo) is a rare example of a simple

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† Tris(diethyldithiocarbamato-*SS'*)nitrosylchromium and bis-[1,2-bis(diphenylphosphino)ethane-*PP'*]fluoronitrosylchromium, respectively.

‡ *Abbreviations used:* dppe = 1,2-bis(diphenylphosphino)ethane; dmpe = 1,2-bis(dimethylphosphino)ethane; dcpe = 1,2-bis(dicyclohexylphosphino)ethane; pdma = *o*-phenylenebis(dimethylarsine); phen = 1,10-phenanthroline; bipy = 2,2'-bipyridyl.

§ In so far as oxidation state has any meaning for transition-metal nitrosyls, (1; M = Cr) may be regarded as a complex of Cr^I. The application of Ibers' rules,[10] for the prediction of linear or bent geometry for MNO groups, gives a 'corrected' value of ν(NO) at 1 707 cm^{-1} indicating the presence of a linear, formally NO^+, nitrosyl ligand.

¶ The formation of (1; M = Mo) from $[Mo(CO)_6]$ and excess of $[NO][PF_6]$ involves, at some stage of the reaction, oxidation of Mo^0 to Mo^I. The oxidant, $[NO]^+$, is reduced to NO gas.

co-ordination complex of Mo^I and is related to $[MoCl_4(NO)(OH_2)]^{2-}$ [12] and $[Mo(CN)_5(NO)]^{3-}$.[9] Its e.s.r. spectrum is similar to that of (1; M = Cr) (Table 2), showing no ligand hyperfine coupling, but the single line is, however, superimposed on a sextet arising from coupling to the spin-active nuclei ^{95}Mo (15.7%) and ^{97}Mo (9.5%) ($I = \frac{5}{2}$).

TABLE 1

Analytical and i.r. data for nitrosyl-chromium and -molybdenum complexes

Complex	Colour	Yield (%)	Analysis [a] (%) C	H	N	I.r. data (cm⁻¹) [b] ν(NO)	ν(CN)
$[Cr(NO)(NCMe)_5][PF_6]_2$	Yellow	92	20.6 (20.8)	2.6 (2.6)	14.6 (14.6)	1 796 [c]	2 327m, 2 305ms [c]
$[Mo(NO)(NCMe)_5][PF_6]_2$	Yellow	64	18.9 (19.3)	2.3 (2.4)	13.2 (13.5)	1 717 [c]	2 320m, 2 292ms [c]
$[Cr(NO)(NCMe)(dppe)_2][BF_4]_2$	Orange-yellow	42	58.7 (59.3)	4.8 (4.7)	2.6 (2.6)	1 691	2272w
$[Mo(NO)(NCMe)(dppe)_2][PF_6]$	Orange-yellow	74	58.3 (58.5)	4.7 (4.6)	2.3 (2.5)	1 597	2 270w
$[Mo(NO)(NCMe)(dppe)_2][PF_6]_2$	Turquoise	92	52.1 (51.7)	4.4 (4.1)	2.1 (2.2)	1 673	2 269w
$[CrCl(NO)(dppe)_2]$	Red	77	68.5 (68.4)	5.5 (5.3)	1.5 (1.5)	1 567	
$[CrCl(NO)(dppe)_2][BF_4]$	Yellow	73	62.2 (62.4)	4.6 (4.8)	1.3 (1.4)	1 667	
$[MoCl(NO)(dppe)_2]$	Yellow	44	65.5 (65.2)	5.4 (5.1)	1.6 (1.5)	1 550br	
$[MoCl(NO)(dppe)_2][PF_6]$	Purple	77	56.3 (56.6)	4.5 (4.4)	1.1 (1.3)	1 641	
$[CrF(NO)(dppe)_2]$	Red	53	69.2 (69.6)	5.5 (5.4)	1.4 (1.6)	1 556	
$[CrF(NO)(dppe)_2][BF_4]$	Yellow	14	63.0 (63.4)	5.0 (4.9)	1.4 (1.4)	1 663	
$[Cr(NO)(S_2CNMe_2)_3]$	Red-brown	53	24.2 (24.4)	4.2 (4.1)	12.6 (12.7)	1 693	1 520
$[Cr(NO)(S_2CNEt_2)_3]$	Red-brown	35	33.8 (34.2)	6.3 (5.7)	10.7 (10.7)	1 685	1 495
$[AsPh_4]_2[Cr(NO)_2\{S_2C_2(CN)_2\}_2]$	Orange-brown	18	57.1 (58.0)	3.8 (3.5)	11.2 (11.1) [d]	1 775, 1 678	2 200ms

[a] Calculated values in parentheses. [b] In CH_2Cl_2 unless stated otherwise. All absorptions strong unless stated m = medium, ms = medium strong, w = weak, or br = broad. [c] In Nujol. [d] Sulphur analysis.

The nitrile ligands of (1) are readily displaced by anionic or neutral ligands. At room temperature in acetone (1; M = Cr) and $Na[S_2CNR_2]\cdot nH_2O$ (R = Me, $n = 2$; R = Et, $n = 3$) afford a dark brown solution from which red-brown crystalline $[Cr(NO)(S_2CNR_2)_3]$ (2; R = Me or Et) can be isolated by column chromatography. The molybdenum complexes $[Mo(NO)(S_2CNR_2)_3]$ [13] are known to have a pentagonal-bipyramidal structure,[14] but the comparative rarity of seven-co-ordination in chromium chemistry [15] and the difference between the ^1H n.m.r. spectrum of (2; R = Me) [τ (CD_2Cl_2) 6.60 (s, 6 H), 6.62 (s, 6 H), 6.69 (s, 3 H), and 6.86 (s, 3 H)] and those of $[M(NO)(S_2CNMe_2)_3]$ (M = Mo [16] or W [17]) suggested fundamental structural dissimilarities. An *X*-ray structural study of (2; R = Et) was therefore carried out.

TABLE 2

E.s.r. data [a] for paramagnetic nitrosyl-chromium and -molybdenum complexes

Complex	$\langle g_{av.}\rangle$	$\langle A_P\rangle$ (G)	$\langle A_N\rangle$ (G)	$\langle A_{Mo}\rangle$ (G)
$[Cr(NO)(NCMe)_5][PF_6]_2$	1.98 [b]			
$[Mo(NO)(NCMe)_5][BF_4]_2$	1.98 [b]			49.0
$[Cr(NO)(NCMe)(dppe)_2][BF_4]_2$	2.00	31.1	1.8 [c] 5.1 [d]	
$[Mo(NO)(NCMe)(dppe)_2][PF_6]_2$	2.02	24.6	2.4 [d]	25.3
$[CrF(NO)(dppe)_2][BF_4]$	2.00	32.7	5.1 [d]	
$[CrCl(NO)(dppe)_2][BF_4]$	2.00	32.7	5.1 [d]	
$[MoCl(NO)(dppe)_2][PF_6]$	2.02	24.8	2.9 [d]	24.8

[a] At room temperature, in CH_2Cl_2 unless stated otherwise. [b] In MeCN. [c] Coupling to ^{14}N of MeCN. [d] Coupling to ^{14}N of nitrosyl ligand.

The *X*-ray diffraction analysis (Tables 3 and 4) confirms the chemical identity of the crystals of (2; R = Et) as $[Cr(NO)(S_2CNR_2)_3]$. Surprisingly, the pentagonal-bipyramidal geometry of $[Mo(NO)(S_2CNR_2)_3]$ is also adopted by the chromium complex (Figure 1); the six sulphur atoms as well as the nitrosyl moiety are arranged about the metal atom.* The nitrosyl ligand and one sulphur atom occupy the axial sites, while the remaining sulphur atoms form the equatorial 'girdle.' Distortions from ideal geometry arise as a consequence of the 'bite' of the diethyldithiocarbamate ligand. The axial sulphur atom, S(1), is significantly bent away from the linear axial position [N(1)–Cr(1)–S(1) 173.7(1)°], and the angle S(1)–Cr(1)–S(2) [113.9(2)°] is somewhat larger than the angles observed in the two other dithiocarbamate ligands [109.0(2) and 109.2(3)°]. Calculation of a least-squares plane through the atoms Cr(1), S(3), S(5), and S(6) gives a root-mean-square (r.m.s.) deviation of less than 0.02 Å. In addition the angles N(1)–Cr(1)–S(3), N(1)–Cr(1)–S(5), and N(1)–Cr(1)–S(6) are all within 2° of a right angle. Both S(2) and S(4) are raised considerably above this plane (by 0.513 and 0.300 Å respectively), the former through the axial positioning of its partner S(1) and the latter presumably as a means of relieving steric pressure in the equatorial girdle.

The Cr–S distances are relatively uniform; the shortest [Cr(1)–S(1) 2.449(1) Å] is to the axial sulphur atom, in complete contrast to $[Mo(NO)(S_2CNBu^n{}_2)_3]$ [14] for which Mo–$S_{ax.}$ (2.568 Å) is longer than Mo–$S_{eq.}$ (average 2.519 Å). The lengthening of the axial Mo–S bond is thought [14,15] to be due to the strong *trans* effect of the nitrosyl ligand. While a similar effect would be expected in (2; R = Et), steric crowding in the equatorial plane, which is more acute than that in $[Mo(NO)(S_2CNR_2)_3]$ because of the inherent relative shortness of Cr–S bonds, will give rise to compensatory lengthening of the Cr–$S_{eq.}$ bonds. Thus, all of the Cr–S bonds (average 2.457 Å) are longer than

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* Of the few known [15] examples of seven-co-ordinate chromium the pentagonal-bipyramidal geometry seems to be preferred.

TABLE 3

Final atomic positions (fractional co-ordinates), with estimated standard deviations in parentheses, for $[Cr(NO)(S_2CNEt_2)_3]$

Atom	*x*	*y*	*z*
Cr(1)	0.803 2(1)	0.096 5(1)	0.239 7(1)
S(1)	0.613 2(1)	0.234 8(1)	0.285 6(1)
S(2)	0.920 3(1)	0.327 8(1)	0.184 7(1)
S(3)	0.777 3(1)	0.047 6(1)	0.071 6(1)
S(4)	0.601 4(1)	−0.120 8(1)	0.208 9(1)
S(5)	0.703 8(1)	−0.010 2(1)	0.386 4(1)
S(6)	0.908 5(1)	0.257 4(1)	0.375 3(1)
N(1)	0 947 6(4)	0.018 5(4)	0.206 1(3)
N(2)	0.732 1(4)	0.501 9(4)	0.243 9(3)
N(3)	0.560 2(4)	0.190 6(4)	0.026 5(3)
N(4)	0.810 6(4)	0.149 2(4)	0.541 1(3)
O(1)	0.048 6(4)	−0.037 4(4)	0.184 9(3)
C(1)	0.751 9(5)	0.372 0(5)	0.238 9(3)
C(2)	0.594 6(6)	0.542 4(4)	0.302 5(4)
C(3)	0.852 8(5)	0.617 1(4)	0.201 6(3)
C(4)	0.850 1(6)	0.612 4(6)	0.097 3(4)
C(5)	0.610 4(9)	0.603 7(7)	0.403 6(5)
C(6)	0.636 0(5)	−0.102 3(4)	0.090 4(3)
C(7)	0.436 2(5)	0.683 2(5)	0.053 9(4)
C(8)	0.598 6(6)	−0.168 9(6)	−0.073 9(3)
C(9)	0.284 8(6)	0.719 6(7)	0.092 0(4)
C(10)	0.698 1(8)	0.730 4(7)	−0.136 8(4)
C(11)	0.809 3(5)	0.135 2(5)	0.449 5(3)
C(12)	0.722 4(6)	0.032 6(6)	0.596 8(3)
C(13)	0.896 7(6)	0.281 9(7)	0.592 1(4)
C(14)	0.798 3(8)	0.383 9(7)	0.644 3(5)
C(15)	0.813 5(7)	−0.068 3(8)	0.596 7(5)

those found in the conventional six-co-ordinate complex $[Cr(S_2CNEt_2)_3]$ [18] (average 2.396 Å). Aside from those dimensions already noted, however, there are no significant inconsistencies between the two compounds $[Cr(S_2CNEt_2)_3]$ and $[Cr(NO)(S_2CNEt_2)_3]$ with respect to the dithiocarbamate ligands. Similarly, the Cr–N [1.681(4) Å] and N–O [1.186(4) Å] distances and the Cr–N–O angle [178.1(3)°] are all within the expected ranges.[6]

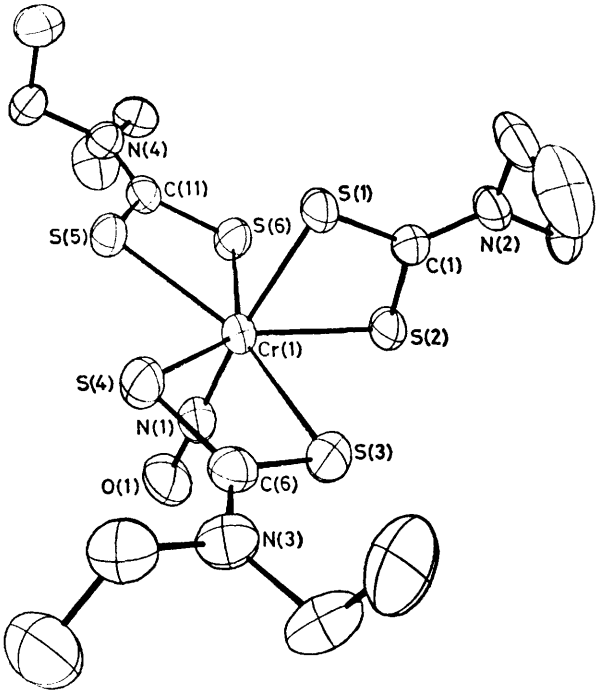

FIGURE 1 Molecular structure of $[Cr(NO)(S_2CNEt_2)_3]$ showing 50% probability ellipsoids of thermal vibration

The earlier [19] incorrect formulation of (1; M = Cr) as *trans*-$[Cr(NO)_2(NCMe)_4]^{2+}$ was largely based on the observation that the reaction with $As(S_2CNEt_2)_3$, as a source of the dithiocarbamate ligand, in boiling $CHCl_3$ or with $Na_2[S_2C_2(CN)_2]$ in acetone afforded the *cis*-dinitrosyls $[Cr(NO)_2(S_2CNEt_2)_2]$ and $[Cr(NO)_2\{S_2C_2(CN)_2\}_2]^{2-}$ respectively. The mass spectrum of (2; R = Et) does not show a parent ion, but a peak at m/e = 408 can be assigned to the ion $[Cr(NO)_2(S_2CNEt_2)_2]^+$, suggesting that *cis*-$[Cr(NO)_2(S_2CNEt_2)_2]$ might be formed thermally from (2; R = Et). Accordingly (2; R = Me) was heated under reflux in toluene and after 3 h only *cis*-$[Cr(NO)_2(S_2CNMe_2)_2]$ and $[Cr(S_2CNMe_2)_3]$ were present in the reaction mixture. The thermal instability of (2) contrasts with the stability of the molybdenum [16] and tungsten [17] analogues for which ^1H n.m.r. spectra have been recorded at temperatures as high as 130 °C.

TABLE 4

Interatomic distances (Å) and angles (°) for $[Cr(NO)(S_2CNEt_2)_3]$

(*a*) Distances

Cr(1)–S(1)	2.449(1)	C(1)–N(2)	1.338(5)
Cr(1)–S(2)	2.452(1)	C(6)–N(3)	1.326(5)
Cr(1)–S(3)	2.459(1)	C(11)–N(4)	1.320(5)
Cr(1)–S(4)	2.461(1)	N–C (single bond):	1.469—1.490 (range) 1.478 (av.)
Cr(1)–S(5)	2.455(1)		
Cr(1)–S(6)	2.468(1)	C–C (single bond):	1.491—1.550 (range) 1.518 (av.)
Cr(1)–N(1)	1.681(4)		
N(1)–O(1)	1.186(4)	S(1)–S(2)	2.884(1)
S(1)–C(1)	1.716(4)	S(2)–S(3)	3.009(1)
S(2)–C(1)	1.723(4)	S(3)–S(4)	2.786(1)
S(3)–C(6)	1.700(4)	S(4)–S(5)	2.876(1)
S(4)–C(6)	1.721(4)	S(5)–S(6)	2.792(1)
S(5)–C(11)	1.713(4)	S(6)–S(2)	3.002(1)
S(6)–C(11)	1.712(4)		

(*b*) Angles

Cr(1)–N(1)–O(1)	178.1(3)	Cr(1)–S(3)–C(6)	91.3(1)
S(1)–Cr(1)–S(2)	72.1(1)	Cr(1)–S(4)–C(6)	90.7(1)
S(1)–Cr(1)–S(3)	90.1(1)	Cr(1)–S(5)–C(11)	91.0(2)
S(1)–Cr(1)–S(4)	88.0(1)	Cr(1)–S(6)–C(11)	90.6(2)
S(1)–Cr(1)–S(5)	92.0(1)	S(1)–C(1)–S(2)	114.0(2)
S(1)–Cr(1)–S(6)	85.5(1)	S(3)–C(6)–S(4)	109.0(2)
S(2)–Cr(1)–S(3)	75.6(1)	S(5)–C(11)–S(6)	109.3(2)
S(3)–Cr(1)–S(4)	69.0(1)	S(1)–C(1)–N(2)	123.4(3)
S(4)–Cr(1)–S(5)	71.6(1)	S(2)–C(1)–N(2)	122.6(3)
S(5)–Cr(1)–S(6)	69.1(1)	S(3)–C(6)–N(3)	126.8(4)
S(6)–Cr(1)–S(2)	75.2(1)	S(4)–C(6)–N(3)	124.2(3)
N(1)–Cr(1)–S(1)	173.7(1)	S(5)–C(11)–N(4)	124.4(2)
N(1)–Cr(1)–S(2)	101.8(1)	S(6)–C(11)–N(4)	126.4(4)
N(1)–Cr(1)–S(3)	89.9(1)	C(2)–N(2)–C(3)	116.4(4)
N(1)–Cr(1)–S(4)	97.9(1)	C(7)–N(3)–C(8)	118.2(3)
N(1)–Cr(1)–S(5)	92.0(1)	C(12)–N(4)–C(13)	117.9(4)
N(1)–Cr(1)–S(6)	91.4(1)	N–C–C:	109.9—112.7 (range) 111.5 (av.)
Cr(1)–S(1)–C(1)	87.0(1)		
Cr(1)–S(2)–C(1)	86.7(1)		

The room-temperature reaction of (1; M = Cr) with $Na_2[S_2C_2(CN)_2]$ in acetone–methanol (1 : 1) gave low yields of *cis*-$[Cr(NO)_2\{S_2C_2(CN)_2\}_2]^{2-}$, analogous to known [20] complexes of Mo and W; a mononitrosyl intermediate related to (2) was not detected.

With PPh_3 or $P(OMe)_3$, (1; M = Cr or Mo) gave a mixture of uncharacterised products although isocyanides and (1; M = Cr) have been shown to yield diamagnetic

$[Cr(CNR)_5(NO)]^+$ (R = Me, Bu^t, or C_6H_4Cl-*p*).[21] With the chelating diphosphine dppe, displacement of four nitrile ligands occurs. In MeCN at room temperature (1; M = Mo, Y = PF_6) and dppe give a deep green solution containing $[M(NO)(NCMe)(dppe)_2]Y_2$ (3; M = Mo, Y = PF_6). On chromatography of the product on alumina, however, the deep green colour of the dication was discharged and elution with CH_2Cl_2 gave an orange solution from which $[M(NO)(NCMe)(dppe)_2]Y$ (4; M = Mo, Y = PF_6) was isolated as orange crystals. The dicationic complex is readily regenerated by treating (4; M = Mo, Y = PF_6) in CH_2Cl_2 with $[N_2C_6H_4F$-*p*$]$-$[PF_6]$, a mild one-electron oxidant, and addition of n-hexane to the deep green solution gives essentially quantitative yields of turquoise (3; M = Mo, Y = PF_6).

TABLE 5

Final atomic positions (fractional co-ordinates), with estimated standard deviations in parentheses, for $[CrF(NO)(dppe)_2]$

Atom	*x*	*y*	*z*
Cr(1)	0.000 0	0.000 0	0.000 0
N(1)	0.160 0	0.975 0	0.050 0
O(1)	0.283 7(6)	−0.043 5(4)	0.090 1(4)
F(1)	0.825 5(5)	0.025 6(3)	0.939 5(3)
P(1)	0.029 9(1)	0.144 1(1)	0.009 9(1)
P(2)	−0.001 3(1)	0.024 5(1)	−0.179 0(1)
C(1)	−0.071 4(4)	0.179 4(2)	−0.124 5(3)
C(2)	−0.030 1(5)	0.135 5(2)	−0.210 6(3)
C(3)	−0.025 6(3)	0.207 8(2)	0.100 8(2)
C(4)	−0.147 1(3)	0.191 6(2)	0.106 0(2)
C(5)	−0.191 8(3)	0.234 7(2)	0.178 0(2)
C(6)	−0.115 0(3)	0.294 1(2)	0.244 9(2)
C(7)	0.006 4(3)	0.310 3(2)	0.239 7(2)
C(8)	0.051 1(3)	0.267 2(2)	0.167 7(2)
C(9)	0.187 0(3)	0.187 8(2)	0.024 7(3)
C(10)	0 294 2(3)	0.151 2(2)	0.098 1(3)
C(11)	0.415 8(3)	0 182 0(2)	0.111 2(3)
C(12)	0.430 2(3)	0.249 2(2)	0.050 9(3)
C(13)	0.323 0(3)	0.285 8(2)	−0.022 5(2)
C(14)	0.201 3(3)	0.255 0(2)	−0.035 6(3)
C(15)	−0.133 0(3)	−0.024 4(2)	−0.283 7(2)
C(16)	−0.116 1(3)	−0.099 4(2)	−0.327 8(2)
C(17)	−0.219 9(3)	−0.138 4(2)	−0.402 2(2)
C(18)	−0.340 7(3)	−0.102 4(2)	−0.432 5(2)
C(19)	−0.357 6(3)	−0.027 4(2)	−0.388 4(2)
C(20)	−0.253 8(3)	0.011 6(2)	−0.314 0(2)
C(21)	0.135 4(4)	0 008 9(2)	−0.224 8(2)
C(22)	0.122 1(4)	0.007 4(2)	−0.334 2(2)
C(23)	0.229 8(4)	−0.000 9(2)	−0.366 2(2)
C(24)	0.350 7(4)	−0.007 7(2)	−0.288 8(2)
C(25)	0.364 0(4)	−0.006 2(2)	−0.179 4(2)
C(26)	0.256 4(4)	0.002 0(2)	−0.147 4(2)

The *trans* disposition of the nitrosyl ligands in both (3; M = Mo) and (4; M = Mo) is unequivocally established by e.s.r. and ^{31}P n.m.r. spectroscopy respectively. Hyperfine coupling of the free electron in (3; M = Mo) to four equivalent phosphorus atoms (^{31}P, $I = \frac{1}{2}$) gives rise to a 1 : 4 : 6 : 4 : 1 quintet each component of which is split into a 1 : 1 : 1 triplet by coupling to the nitrosyl-nitrogen atom (^{14}N, $I = 1$); satellites due to coupling to the spin-active molybdenum nuclei (^{95}Mo, ^{97}Mo) may be observed (Table 2). The ^{31}P n.m.r. spectrum of (4; M = Mo, Y = PF_6) gives only one line (−59.0 p.p.m. in CH_2Cl_2–$CDCl_3$), apart from the septet due to the $[PF_6]^-$ anion, verifying the equivalence of the dppe ligands.

The reaction of dppe with (1; M = Cr) occurs less readily than with (1; M = Mo) but in refluxing MeCN a mixture of paramagnetic species, separable by chromatography on alumina, is formed. The first, (orange) complex is (3; M = Cr) with an e.s.r. spectrum (Table 2) similar to that of the molybdenum analogue but showing additional hyperfine coupling to the nitrile-nitrogen atom. The second product is a yellow-orange crystalline salt (5; M = Cr) which also shows the e.s.r. spectrum (Table 2) typical of the $M(NO)(dppe)_2$ group found in (3; M = Cr or Mo). On reduction with $Na[BH_4]$ in tetrahydrofuran (thf), (5; M = Cr) affords a neutral, diamagnetic, red crystalline solid (6; M = Cr) which may be re-oxidised, by $[N_2C_6H_4F$-*p*$]Y$ (Y = BF_4 or PF_6) in CH_2Cl_2, to (5; M = Cr). That (5; M = Cr) and (6; M = Cr) are interconvertible *via* a one-electron redox process (confirmed by electrochemical studies detailed below), and that (6; M = Cr) is neutral and diamagnetic, suggest (5; M = Cr) to be $[CrX(NO)(dppe)_2]Y$ with X a monoanionic one-electron donor. Unfortunately, the nature of X could not be established by conventional methods and a single-crystal *X*-ray diffraction study of (6; M = Cr) was therefore carried out.

The *X*-ray diffraction analysis (Tables 5 and 6) establishes the presence of two mutually *trans* diphosphine ligands and the NO group, and strongly suggests the axial ligand X to be fluoride (Figure 2). The geometry associated with the dppe ligands conforms with that found for $[Cr(CO)_4(dppe)]$[22] in every respect. Notable features are the bending of the phenyl rings away from the metal atom [Cr–P–C(phenyl) (average) 120.2°] and the puckering of the P–C–C–P chain.

TABLE 6

Interatomic distances (Å) and angles (°) for $[CrF(NO)(dppe)_2]$

(*a*) Distances

Cr(1)–F(1)	1.880(5)	C(1)–C(2)	1.530(5)
Cr(1)–N(1)	1.725	C(2)–P(2)	1.865(4)
N(1)–O(1)	1.331	P(1)–C(3)	1.835(3)
Cr(1)–P(1)	2.378(1)	P(1)–C(9)	1.831(3)
Cr(1)–P(2)	2.380(1)	P(2)–C(15)	1.827(3)
P(1)–C(1)	1.846(4)	P(2)–C(21)	1.822(4)

(*b*) Angles

Cr(1)–N(1)–O(1)	179.0	Cr(1)–P(2)–C(15)	114.4(1)
N(1)–Cr(1)–F(1)	177.5	Cr(1)–P(2)–C(21)	124.5(1)
P(1)–Cr(1)–F(1)	84.7(1)	C(2)–P(2)–C(15)	102.8(2)
P(1)–Cr(1)–N(1)	96.1	C(2)–P(2)–C(21)	99.4(2)
P(1)–Cr(1)–P(2)	81.0(1)	C(15)–P(2)–C(21)	103.6(1)
Cr(1)–P(1)–C(1)	103.1(1)	P(1)–C(3)–C(4)	117.3(1)
Cr(1)–P(1)–C(3)	121.8(1)	P(1)–C(3)–C(8)	122.6(1)
Cr(1)–P(1)–C(9)	120.2(1)	P(1)–C(9)–C(10)	118.1(1)
C(3)–P(1)–C(9)	102.7(1)	P(1)–C(9)–C(14)	121.9(1)
C(1)–P(1)–C(9)	103.8(2)	P(2)–C(15)–C(16)	120.9(1)
C(1)–P(1)–C(3)	102.5(2)	P(2)–C(15)–C(20)	119.0(1)
P(1)–C(1)–C(2)	109.0(3)	P(2)–C(21)–C(22)	121.6(1)
C(1)–C(2)–P(2)	111.3(3)	P(2)–C(21)–C(26)	118.3(1)
Cr(1)–P(2)–C(2)	109.2(1)		

C–C bond distances within the phenyl rings were fixed at 1.395 Å with C–C–C angles of 120°.

Unequivocal proof of the identity of X is hampered by inherent disorder in the molecule, resulting from the crystallographically imposed centre of symmetry. Refinement of the axial atoms N, O, and X proceeded with difficulty but was most satisfactory, with regard to the relative electron densities of the peaks in the axial region, for X as a fluoride ion. Attempts to verify the assignment by ^{19}F n.m.r. spectra were fruitless but the synthesis of (5; M = Cr), from (1; M = Cr), and the formation of (6; M = Cr) by tetrahydroborate reduction of (3; M = Cr) also suggest fluoride, from $[BF_4]^-$ or $[PF_6]^-$, to be the axial ligand X.

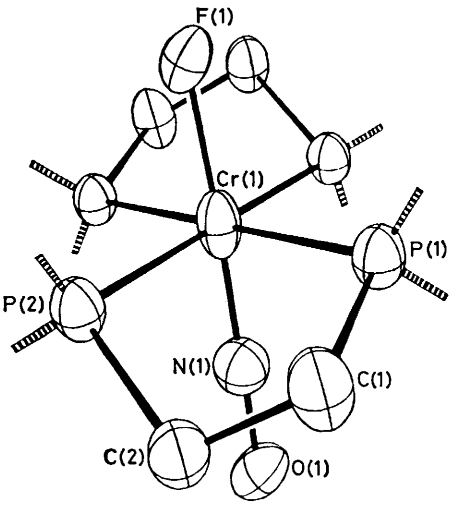

FIGURE 2 Molecular structure of $[CrF(NO)(dppe)_2]$, showing 50% probability ellipsoids of thermal vibration. The phenyl rings of the dppe ligands are omitted for clarity

Analogues of (6; X = F or Br, M = Mo; X = F, Cl, or Br, M = W) have recently been reported [23,24] and the chloro-complexes (5; M = Cr or Mo, X = Cl) and (6; M = Cr or Mo, X = Cl) are readily prepared by nitrile displacement from (3) or (4) by chloride ion. Thus bis(triphenylphosphine)iminium chloride and (3) in MeCN afford paramagnetic, monocationic, orange (5; M = Cr, X = Cl) or purple (5; M = Mo, X = Cl). The latter is better prepared, however, by $[N_2C_6H_4F\text{-}p]Y$ (Y = BF_4 or PF_6) oxidation of the yellow diamagnetic complex (6; M = Mo, X = Cl) which results from chloride displacement of the nitrile ligand of (4; M = Mo, X = Cl). The red chromium compound (6; M = Cr, X = Cl) can only be prepared by tetrahydroborate reduction of (5; M = Cr, X = Cl) in thf.

TABLE 7

Cyclic voltammetric data [a] for nitrosyl-chromium and -molybdenum complexes

Complex	E_p/V	$(E_p)_{ox} - (E_p)_{red}$ mV	$(E_p)_{ox} - (E_{p/2})_{ox}$ mV	$(E_p)_{red} - (E_{p/2})_{red}$ mV	$(i_p)_{ox}/(i_p)_{red}$
$[Cr(NO)(NCMe)(dppe)_2][BF_4]_2$	−0.03,	60	65	60	1.04
	−0.06 [b]	60	64	62	1.04
$[Mo(NO)(NCMe)(dppe)_2][PF_6]$	0.35	64	66	66	1.00
$[Mo(NO)(NCMe)(dppe)_2][PF_6]_2$	0.35	60	60	58	1.04
$[CrF(NO)(dppe)_2]$	−0.53	60	62	62	0.97
$[CrF(NO)(dppe)_2][BF_4]$	−0.55,	60	64	62	1.04
	−0.50 [b]	67	69	62	1.06
$[CrCl(NO)(dppe)_2]$	−0.43	62	69	66	1.01
$[CrCl(NO)(dppe)_2][BF_4]$	−0.45	60	87	65	1.07
$[MoCl(NO)(dppe)_2]$	−0.02	62	63	62	0.96
$[MoCl(NO)(dppe)_2][PF_6]$	−0.02	60	63	59	1.04

[a] In CH_2Cl_2, 0.05 mol dm^{-3} in $[NEt_4][ClO_4]$. [b] In MeCN, 0.1 mol dm^{-3} in $[NEt_4][ClO_4]$.

The structures of (5; X = Cl) and (6; X = Cl) are related to those of (3) and (4) respectively; the e.s.r. spectra of (5; M = Cr or Mo, X = Cl) show the familiar 15-line pattern due to coupling of the unpaired electron with the four equivalent phosphorus atoms and the nitrosyl-nitrogen atom, and the ^{31}P n.m.r. spectrum of (6; M = Cr) (−21.1 p.p.m. in CH_2Cl_2–CD_2Cl_2) or (6; M = Mo) (−52.2 p.p.m. in CH_2Cl_2–$CDCl_3$) shows only one singlet resonance. The complexes $[CrCl(NO)(pdma)_2]^z$ (z = 0 and +1) have been described [25] and once again the e.s.r. spectrum of the monocation establishes a *trans*-nitrosylchloride structure.

The reaction between (3; M = Cr, Y = BF_4 or PF_6) and LiCl or $[N(PPh_3)_2]Cl$ in refluxing acetone results in colour changes from orange to brown, and finally to the deposition of green, paramagnetic, nitrosyl-containing products. Although full characterisation has not been possible the i.r. spectra (Nujol) of the green solids show, in each case, one nitrosyl absorption [ν(NO) at 1 665 cm^{-1}] and the absence of the anion Y^-. In CH_2Cl_2, the e.s.r. spectrum, centred at $\langle g_{av.}\rangle = 2.00$, shows a 1 : 2 : 1 triplet, suggesting the presence of two equivalent phosphorus atoms ($\langle A_p \rangle$ = 27.1 G),* further split into 1 : 1 : 1 triplets ($\langle A_{NO} \rangle$ = 5.6 G). The complexes are tentatively formulated as salts containing the anion $[CrCl_3(NO)(dppe)]^-$.

Electrochemical Studies.—The chemical oxidation and reduction reactions described above also occur electrochemically at the platinum electrode. In CH_2Cl_2, complexes (3)—(6) undergo reversible one-electron transfer as shown by the close proximity of the values $(E_p)_{ox} - (E_p)_{red}$, $(E_p)_{ox} - (E_{p/2})_{ox}$ or $(E_p)_{red} - (E_{p/2})_{red}$, and $(i_p)_{ox}/(i_p)_{red}$ to 60 mV, 57 mV, and unity respectively (Table 7). As further evidence for the full chemical reversibility of the redox process the oxidation potentials of redox-related pairs [*e.g.* (3) and (4), M = Mo] are equal within experimental error. There is a marked dependence of E_p on the central metal atom and on the overall charge of the complex. The molybdenum complexes are oxidised at a potential *ca.* 0.4 V more positive than the chromium analogues; for a given metal the neutral halogeno-com-

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* Throughout this paper: 1 G = 10^{-4} T.

pounds (6; X = F or Cl) are more readily oxidised, by about 0.4 V, than the isoelectronic monocationic nitrile derivatives (4).

By contrast to (4) and (6), the complexes *cis*-$[M(CO)_2\{Ph_2P(CH_2)_nPPh_2\}_2]$ (M = Cr, Mo, or W; *n* = 1—3),[26] $[MBr(CO)_3L_2]$ (M = Mn or Re, L = P-, As-, or Sb-donor),[27] and *cis*-$[M(CO)_4(carbene)_2]$ (M = Mo or W, carbene = 2,4-dimethyl-1,2,4-triazolin-3-ylidene) [28] undergo geometrical isomerisation on one-electron oxidation. Recent calculations [29] suggest that the structures adopted by the oxidised and reduced forms of octahedral complexes depend on the π-donor or -acceptor properties of the ligands present. Thus $[Mo(CO)_2(PH_3)_4]$, containing π-accepting carbonyl ligands, has the *cis* structure which will isomerise to the ***trans*** form on oxidation. By contrast, $[MoO_2(PH_3)_4]$, with two π-donor oxo-ligands, will have the ***trans*** configuration in both oxidised and reduced states. Although the nitrosyl ligand of (4) or (6) is a strong π-acceptor the second ligand, L [nitrile (4) or halogen (6)], has no such properties and, on balance, the ***trans***-(NO)L structure is adopted and maintained during electron transfer.

The isocyanide complexes $[Cr(CNR)_5(NO)]^+$ (R = Me, Bu^t, or C_6H_4Cl-*p*) [21] not only undergo electrochemical oxidation to dications but also to the unstable tricationic species $[Cr(CNR)_5(NO)]^{3+}$. The cyclic voltammograms of (3; M = Cr) and (5: M = Cr, X = F; M = Mo, X = Cl) provide some evidence for a second electron-transfer step but the proximity of the oxidation wave to the curve of the base electrolyte precluded further study.

The complexes (1; M = Cr or Mo) are insoluble in CH_2Cl_2 but undergo ill defined reduction processes in MeCN. For (1; M = Cr) a reduction wave at *ca.* —0.6 V (scan rate = 200 mV s^{-1}), with no corresponding oxidation peak on the reverse sweep of the cyclic voltammogram, is indicative of irreversible one-electron transfer. For (1; M = Mo) the reduction, at —0.42 V, has $(i_p)_{ox}/(i_p)_{red} = 1.03$, but $(E_p)_{ox} - (E_p)_{red} = 180$ mV implying electrochemical irreversibility at 200 mV s^{-1}. In addition, at slower scan rates the oxidation peak diminishes in height. Although there is no good evidence for the reduction products $[M(NO)(NCMe)_5]^+$ (M = Cr or Mo), analogues, namely $[M(CN)_5(NO)]^{4-}$ (M = Cr [30] and Mo [9]), are known. In addition, the identity of $[MCl_5(NO)]^{2-}$, isoelectronic with species which might be formed by one-electron oxidation of (1), (3), or (5), is well established.[31-33]

Finally, (2; R = Me or Et) did not undergo oxidation or reduction in the range ± 1.5 V. This behaviour contrasts markedly with that of the related arenediazo-complex $[Mo(N_2C_6H_4R)(S_2CNMe_2)_3]$ (R = *o*-, *m*-, or *p*-substituents) which undergoes reversible one-electron oxidation at a platinum or vitreous carbon electrode; [34] the purple monocation has been generated by controlled-potential electrolysis. A second wave, corresponding to the irreversible one-electron oxidation of the monocation to an unstable dication, is also observed in the cyclic voltammogram. In addition $[MoL(S_2CNMe_2)_3]$ (L = NO or NS) undergoes irreversible one-electron oxidation at *ca.* 1.1 V (*vs.* a saturated calomel electrode).

EXPERIMENTAL

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Unless otherwise stated the solid complexes are air-stable and soluble in polar solvents such as acetone, CH_2Cl_2, and acetonitrile to give solutions which are stable under nitrogen. All the solvents used were dried by standard methods and deoxygenated before use. Nitrosonium salts were purchased from Fluorochem Ltd., Glossop, Derbyshire, and arenediazonium salts were prepared by a published method.[35]

Infrared spectra were recorded on Perkin-Elmer PE257 or 457 spectrophotometers and calibrated against the absorption band of polystyrene at 1 601 cm^{-1}. Proton n.m.r. spectra were obtained on a Varian Associates HA100 spectrometer and calibrated against tetramethylsilane as internal reference, ^{31}P spectra on a JEOL PFT100 spectrometer and calibrated against 85% aqueous H_3PO_4 as external reference. *X*-Band e.s.r. spectra were recorded on a Varian Associates 4502/15 instrument and calibrated against a solid sample of the diphenylpicrylhydrazyl (dpph) radical. Cyclic voltammetry was carried out using the positive feedback capacity of the AMEL Electrochemolab in conjunction with a three-electrode cell. Auxiliary and working electrodes were platinum wire and the reference was a calomel electrode (1 mol dm^{-3} in LiCl). Solutions were 10^{-3} mol dm^{-3} in complex and either 0.05 mol dm^{-3} (in CH_2Cl_2) or 0.1 mol dm^{-3} (in MeCN) in $[NEt_4][ClO_4]$ as supporting electrolyte. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Pentakis(acetonitrile)nitrosylchromium Bis(hexafluorophosphate), $[Cr(NO)(NCMe)_5][PF_6]_2$.—To a stirred suspension of $[Cr(CO)_6]$ (0.55 g, 2.5 mmol) in MeCN (20 cm^3) was added solid $[NO][PF_6]$ (1.83 g, 10.5 mmol). After gas evolution had ceased (10 min) the brown solution was filtered and diethyl ether (50 cm^3) added. The yellow precipitate was recrystallised from MeCN–diethyl ether to give the yellow product, yield 1.32 g (92%). The complex is soluble in acetone or acetonitrile to give yellow air-sensitive solutions; the solid slowly decomposes in air and is best stored ***in vacuo***.

Pentakis(acetonitrile)nitrosylmolybdenum Bis(hexafluorophosphate), $[Mo(NO)(NCMe)_5][PF_6]_2$.—The reaction of $[Mo(CO)_6]$ (0.52 g, 2 mmol) and $[NO][PF_6]$ (0.90 g, 5.2 mmol) in MeCN (60 cm^3) was carried out as above but with a vigorous stream of nitrogen passed ***through*** the solution. The addition of diethyl ether (120 cm^3) to the mixture, after 30 min, gave a pale green precipitate which was recrystallised from MeCN–diethyl ether to give the product as a yellow solid, 0.80 g (64%). The solid complex visibly darkens in 24 h even on storage ***in vacuo***.

Tris(dimethyldithiocarbamato)nitrosylchromium, $[Cr(NO)(S_2CNMe_2)_3]$.—To a stirred solution of $[Cr(NO)(NCMe)_5][BF_4]_2$ (0.58 g, 1.26 mmol) in acetone (25 cm^3) was added $Na[S_2CNMe_2]\cdot 2H_2O$ (0.54 g, 3.0 mmol). After 15 min the brown solution was evaporated to dryness (at room temperature) and the residue extracted with a minimum volume of $CHCl_3$. Chromatography on an alumina–$CHCl_3$ column gave a brown band, eluted with $CHCl_3$, which when reduced in volume and treated with n-hexane gave the product as a red-brown *solid*, yield 0.23 g (53%). The complex [Cr(NO)-

$(S_2CNEt_2)_3]$ was prepared by the same method (35%). Both complexes are soluble in $CHCl_3$ but only poorly so in acetone.

Thermolysis of $[Cr(NO)(S_2CNMe_2)_3]$.—A solution of $[Cr(NO)(S_2CNMe_2)_3]$ (0.28 g, 0.63 mmol) in toluene (15 cm^3) was heated under reflux for 3 h. The resulting purple solution was then reduced in volume and hexane added to precipitate $[Cr(S_2CNMe_2)_3]$ (0.19 g) as a blue crystalline solid. After removal of the solid by filtration the filtrate was reduced in volume and chromatographed on a CH_2Cl_2–alumina column. Elution of the pink band with CH_2Cl_2 and evaporation to dryness gave $[Cr(NO)_2(S_2CNMe_2)_2]$ (0.05 g) as a purple solid.

Bis(tetraphenylarsonium) Bis(cis-*1,2-dicyanoethylene-1,2-dithiolato)dinitrosylchromium*, $[AsPh_4]_2[Cr(NO)_2\{S_2C_2(CN)_2\}_2]$.—To $[Cr(NO)(NCMe)_5][PF_6]_2$ (0.30 g, 0.52 mmol) in acetone (10 cm^3) was added a solution of $Na_2[S_2C_2(CN)_2]$ (0.19 g, 1.0 mmol) in methanol (10 cm^3). After stirring for 15 min, $[AsPh_4]Cl$ (0.84 g, 2.0 mmol) in ethanol (20 cm^3) was added to the dark brown solution. Partial evaporation of the solvent gave a brown solid which was recrystallised twice from acetone–water to give the solid orange-brown product, 0.1 g (17% based on Cr, 34% based on NO).

Reaction of $[Cr(NO)(NCMe)_5][BF_4]_2$ *with 1,2-Bis(diphenylphosphino)ethane*.—A mixture of $[Cr(NO)(NCMe)_5][BF_4]_2$ (2.0 g, 4.3 mmol) and dppe (4.4 g, 11.0 mmol) in MeCN (40 cm^3) was heated under reflux for 20 min. The resulting orange-red solution was evaporated to dryness, the residue dissolved in a minimum volume of CH_2Cl_2, and chromatographed on an alumina–CH_2Cl_2 column. Elution with CH_2Cl_2 gave a yellow band which, on addition of n-hexane and partial removal of solvent *in vacuo*, gave $[CrF(NO)(dppe)_2][BF_4]$ as orange-yellow crystals, yield 0.6 g (14%). Elution with MeCN gave an orange band which, on evaporation to low volume and addition of diethyl ether, gave $[Cr(NO)(NCMe)(dppe)_2][BF_4]_2$ as orange crystals, yield 2.0 g (42%).

Bis[1,2-bis(diphenylphosphino)ethane]fluoronitrosylchromium, $[CrF(NO)(dppe)_2]$.—To a stirred suspension of $[CrF(NO)(dppe)_2][BF_4]$ (0.5 g, 0.51 mmol) in thf (30 cm^3) was added $Na[BH_4]$ (0.05 g, 1.3 mmol). After 2 h the red solution was evaporated to dryness and the residue recrystallised from CH_2Cl_2–n-hexane to give the product as red *crystals*, yield 0.24 g (53%).

Acetonitrilebis[1,2-bis(diphenylphosphino)ethane]nitrosylmolybdenum Hexafluorophosphate, $[Mo(NO)(NCMe)(dppe)_2][PF_6]$.—The salt $[Mo(NO)(NCMe)_5][PF_6]_2$ (3.1 g, 5.0 mmol) and dppe (5.0 g, 12.6 mmol) were stirred in MeCN (50 cm^3) for 1 h. The resulting deep green solution was evaporated to dryness and redissolved in a minimum volume of CH_2Cl_2. On chromatography on an alumina–CH_2Cl_2 column the dark green band slowly became orange and was eluted with CH_2Cl_2 as an orange solution. Evaporation to low volume (*ca.* 15 cm^3) and addition of hexane gave the product as an orange-yellow *solid*, yield 4.1 g (74%).

Acetonitrilebis[1,2-bis(diphenylphosphino)ethane]nitrosylmolybdenum Bis(hexafluorophosphate), $[Mo(NO)(NCMe)(dppe)_2][PF_6]_2$.—To $[Mo(NO)(NCMe)(dppe)_2][PF_6]$ (1.1 g, 1.0 mmol) in CH_2Cl_2 (50 cm^3) was added $[N_2C_6H_4F\text{-}p][PF_6]$ (0.27 g, 1.0 mmol). After stirring for 30 min the deep turquoise solution was filtered, reduced in volume, and treated with n-hexane to give the product as a turquoise *solid*, yield 1.15 g (92%).

Bis[1,2-bis(diphenylphosphino)ethane]chloronitrosylchromium Tetrafluoroborate, $[CrCl(NO)(dppe)_2][BF_4]$.—A solution of $[Cr(NO)(NCMe)(dppe)_2][BF_4]_2$ (0.34 g, 0.3 mmol) and $[N(PPh_3)_2]Cl{\cdot}0.5CH_2Cl_2$ (0.19 g, 0.3 mmol) in CH_2Cl_2 (20 cm^3) was heated under reflux for 1 h. Evaporation of the resulting orange solution to low volume followed by chromatography on an alumina–CH_2Cl_2 column gave a yellow band. Elution with acetone–CH_2Cl_2 (3 : 7), evaporation to low volume, and addition of diethyl ether gave a bright yellow solid which was recrystallised from CH_2Cl_2–diethyl ether, yield 0.22 g (73%).

Bis[1,2-bis(diphenylphosphino)ethane]chloronitrosylchromium, $[CrCl(NO)(dppe)_2]$.—To a stirred suspension of $[CrCl(NO)(dppe)_2][BF_4]$ (0.1 g, 0.1 mmol) in thf (30 cm^3) was added $Na[BH_4]$ (0.04 g, 1.0 mmol). After 5 h the red solution was evaporated to dryness and the residue recrystallised from CH_2Cl_2–n-hexane to give the product as a red *solid*, 0.07 g (77%).

Bis[1,2-bis(diphenylphosphino)ethane]chloronitrosylmolybdenum, $[MoCl(NO)(dppe)_2]$.—A solution of $[Mo(NO)(NCMe)(dppe)_2][PF_6]$ (1.0 g, 0.9 mmol) and $[N(PPh_3)_2]Cl{\cdot}0.5CH_2Cl_2$ (0.55 g, 0.9 mmol) in CH_2Cl_2 (50 cm^3) was heated under reflux for 90 min. The yellow solution was evaporated to low volume and chromatographed on an alumina–CH_2Cl_2 column. Elution of the yellow band with CH_2Cl_2, reduction of the eluate in volume, and treatment with n-hexane gave the product as a bright yellow *solid*, yield 0.4 g (44%).

Bis[1,2-bis(diphenylphosphino)ethane]chloronitrosylmolybdenum Hexafluorophosphate, $[MoCl(NO)(dppe)_2][PF_6]$.—To a stirred solution of $[MoCl(NO)(dppe)_2]$ (0.45 g, 0.47 mmol) in CH_2Cl_2 (20 cm^3) was added $[N_2C_6H_4F\text{-}p][PF_6]$ (0.13 g, 0.47 mmol). After 10 min the purple solution was evaporated to low volume and chromatographed on an alumina-CH_2Cl_2 column. The blue band was eluted with CH_2Cl_2, reduced in volume, and treated with n-hexane to precipitate a dark blue solid. Recrystallisation from acetone–diethyl ether gave the product as a purple *solid*, yield 0.4 g (77%).

Structure Determinations.—(*a*) $[Cr(NO)(S_2CNEt_2)_3]$. The crystal of $[Cr(NO)(S_2CNEt_2)_3]$ chosen for intensity measurements (0.36 × 0.12 × 0.04 mm) was mounted and aligned on a Syntex *P*3 four-circle diffractometer according to methods defined earlier.[36] Of 4 591 independent observations, 3 033 satisfied the criterion $F \geqslant 6\sigma(F)$ and only these were used in the solution and refinement of the structure.

Crystal data. $C_{15}H_{30}CrN_4OS_6$, $M = 526.6$, Triclinic, space group $P\bar{1}$, $a = 9.525(3)$, $b = 9.903(5)$, $c = 14.649(7)$ Å, $\alpha = 103.8(4)$, $\beta = 74.5(3)$, $\gamma = 107.4(3)°$, $U = 1\,251.7(9)$ Å^3, $D_m = 1.38$ g cm^{-3}, $Z = 2$, $D_c = 1.40$ g cm^{-3}, $F(000) = 552$, Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 9.0 cm^{-1}.

After an absorption correction, the structure was solved by conventional heavy-atom methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were incorporated in fixed positions where this was possible (C–H 1.08 Å). In the methyl groups, where this was not possible, free rotation about the carbon–carbon bond was allowed with the C–H distances and the H–C–H angles held at sensible values. Weights were then incorporated according to the scheme $w = 1.30/[\sigma^2(F) + 0.000\,7F^2]$ to equate, as nearly as possible, the sums of the variances $(\Sigma w\Delta F^2)$ for different classes of reflections.

The refinement converged at $R = 0.040$ and $R' = 0.042$. The final electron-density difference synthesis showed no peaks >0.5 and < -0.5 e Å^{-3}.

(*b*) $[CrF(NO)(dppe)_2]$. The crystal of $[CrF(NO)(dppe)_2]$ chosen for intensity measurements (0.40 × 0.20 × 0.20 mm) was mounted on a Syntex $P2_1$ four-circle diffractometer as above.[36] Of 4 005 measured intensities ($2\theta < 50°$) 2 633 were deemed observed according to the criterion $F \geqslant 6.0\sigma(F)$.

Crystal data. $C_{52}H_{48}CrFNOP_4$, $M = 896.9$, Monoclinic space group $P2_1/n$, $a = 11.080(6)$, $b = 16.352(6)$, $c = 13.129(7)$ Å, $\beta = 109.17(4)°$, $U = 2\,247(2)$ Å^3, $D_m = 1.33$ g cm^{-3}, $Z = 2$, $D_c = 1.32$ g cm^{-3}, $F(000) = 936$, Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 4.0 cm^{-1}.

The structure was solved by conventional heavy-atom methods and all but the two *trans*-axial ligands were rapidly located ($R = 0.21$). The position of the metal atom, at the centre of symmetry, necessitates a 50% disordering of each of the *trans* ligands. An electron-density difference map, with phasing based on the positions of all but the above mentioned *trans* ligands, revealed mutually *trans* peaks 1.8 Å from the chromium atom (7.6 e Å^{-3}) and further peaks beyond these (3.5 e Å^{-3}). These peaks were assigned to one half of a linear nitrosyl ligand, known to be present in the molecule, and half of a fluorine atom.

The nitrosyl oxygen atom was incorporated into the atom list and refined with anisotropic thermal parameters, as were the other non-hydrogen atoms. The close proximity of the disordered nitrogen and fluorine atoms required alternate refinement of the two, but the nitrogen atom was eventually fixed, with a Cr–N distance of 1.725 Å, and only an isotropic thermal parameter for this atom was incorporated. The hydrogen atoms of the phenyl rings (C–H 1.08 Å, C–C–H 120°) and CH_2 (C–H 1.08 Å, C–C–H 109.5°) groups were fixed at expected positions and their thermal parameters tied to a common variable. Weights were applied according to the scheme $w = 0.042\,3/[\sigma^2(F) + 0.00\,1F^2]$. The refinement converged at $R = 0.047$ and $R' = 0.052$ and a final electron-density synthesis showed no peaks >0.3 or < -0.4 e Å^{-3}. With a linear absorption coefficient of 4.0 cm^{-1} an absorption correction was deemed unnecessary.

For both structural determinations atomic scattering factors for non-hydrogen atoms were taken from ref. 37 with corrections for anomalous dispersion for chromium from ref. 38. Scattering factors for hydrogen were from ref. 39. All computational work was carried out at the South Western Universities Computation Centre with the program SHELX-76.[40] Observed and calculated structure factors, thermal parameters, and positional parameters for the hydrogen atoms are listed in Supplementary Publication No. SUP 22846 (34 pp.).*

We thank the S.R.C. for a Studentship (to S. C.), for a Research Assistantship (to G. E. T.), and for funds to purchase electrochemical equipment (N. G. C.).

[0/243 *Received*, 11*th February*, 1980]

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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