Complexes of Molybdenum-(II) and -(IV) and Tungsten(II) with Sterically Hindered Thiolate Ligands. Synthesis, Reactivity, and *X*-Ray Crystal Structures of $[PPh_4][Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_3(CO)_2]$ and $[Mo(NNPh)(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NCMe)]$[‡]

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$[MBr_2(CO)_4]$ (M = Mo or W) react with thiolate anions SR^- to give the anions $[M(SR)_3(CO)_2]^-$ (SR = $SC_6H_2Pr^i_3$-2,4,6, $SC_6H_3Pr^i_2$-2,6, SC_6H_2Br-4-Pr^i_2-2,6, $SC_6H_2Me_3$-2,4,6, SC_6F_5). The complex $[PPh_4][Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_3(CO)_2]$ crystallises in space group $P\bar{1}$ with $a = 13.451(2)$, $b = 14.229(2)$, $c = 19.862(3)$ Å, $\alpha = 96.11(1)$, $\beta = 94.11(1)$, $\gamma = 111.04(1)°$, and $Z = 2$. Structure analysis based on 2 939 reflections with $I_o > 3.0\sigma(I_o)$ refined to $R = 0.0755$. The anion has a trigonal-bipyramidal structure with axial co-ligands. The complexes $[M(SR)_3(CO)_2]^-$ react with CO to give $[M(SR)_3(CO)_3]^-$. $[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_3(CO)_2]^-$ reacts with neutral donors L to give $[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_3(CO)L]^-$ (L = MeCN, Bu^tCN, PMe_2Ph, or Bu^tNC) and with $[N_2Ph][BF_4]$ in MeCN to give $[Mo(NNPh)(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NCMe)]$. This complex crystallises in space group *Pnma* with $a = 9.962(3)$, $b = 21.002(4)$, $c = 27.646(4)$ Å, and $Z = 4$. Structure analysis based on 1 772 reflections with $I_o > 3\sigma(I_o)$ refined to $R = 0.075$. The NNPh and MeCN ligands occupy the axial sites of a trigonal bipyramid with the thiolates equatorial.

The reduction of dinitrogen to ammonia by the enzyme nitrogenase is now believed to occur at a molybdenum site which is itself part of an iron–molybdenum–sulphur cluster (Fe–Mo co-factor). Attempts to model the reactivity of Fe–Mo co-factor towards small molecules and in particular using complexes containing molybdenum with sulphido- or thiolato-ligands have been largely unsuccessful. A notable exception has been the recent report of a mononuclear Fe_3MoS_4-type cluster which binds CO and other alternative nitrogenase substrates.[1] The prevalent tendency in metal–sulphur chemistry is the formation of polymeric sulphur bridged species, the bridging atoms occupying sites otherwise available for catalysis and the binding of small molecules. Aliphatic thiols frequently undergo C–S bond cleavage on reaction with metal ions[2,3] leading to the formation of relatively inert sulphido-bridged polymers. We have attempted to avoid these problems by using aromatic thiolate ligands with *ortho*-substituents which offer steric inhibition to sulphur bridging. Examples of the thiols used and their abbreviations are given in Figure 1.

We here report the preparation and structural characterisation of a series of mononuclear Mo^{II} and W^{II} trigonal-bipyramidal complexes with equatorial thiolates and a range of π-acceptor molecules in the axial sites. Some related nitrosyl complexes of simple arenethiolates with molybdenum and tungsten were reported earlier,[4] and sterically-hindered thiolate derivatives of ruthenium,[5] iron,[6] and osmium[5] have been described.

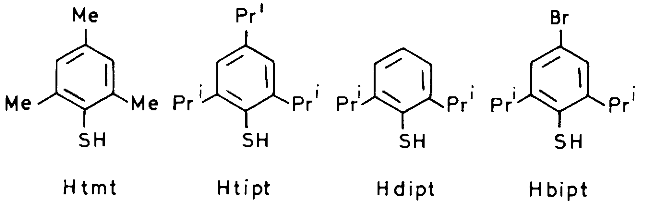

Figure 1. Sterically hindered arenethiolates and their abbreviations

Some of this work has been published earlier in preliminary form.[7]

Results and Discussion

Synthesis and Characterisation of the Complexes $[PPh_4][M(SR)_3(CO)_2]$ (M = Mo *or* W; SR = *Arenethiolate*).—The anion $[M(SR)_3(CO)_2]^-$ can be prepared by reaction of $[MBr_2(CO)_4]$ (M = Mo or W) with three equivalents of the appropriate thiol RSH (SR = tmt, tipt, dipt, bipt, or C_6F_5S, M = Mo; SR = tmt, tipt, or dipt, M = W) in methanol at room temperature in the presence of triethylamine. The complexes are conveniently isolated as crystalline $[PPh_4]^+$ salts by the addition of $[PPh_4]Br$. If the above reaction is carried out with thiophenol a brown unstable material is obtained, and its complex i.r. spectrum suggests a polymeric thiolato-bridged structure. Under the same conditions pentafluorothiophenol gives the pink anion $[Mo(SC_6F_5)_3(CO)_2]^-$.

The bis(carbonyl) complexes can also be synthesised less conveniently by reaction of $[MCl_4(thf)_2]$ (M = Mo or W, thf = tetrahydrofuran) with the sodium salt of the thiol in thf under 1 atm of carbon monoxide. The thiol acts as a reducing agent and the aryl disulphide formed can be isolated from the reaction mixture and identified by its melting point.

The physical properties and analytical data for the complexes are summarised in Table 1 together with selected i.r. and u.v. spectroscopic data. The complexes are diamagnetic, crystalline solids which are stable in air for several hours before de-

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[‡] Tetraphenylphosphonium dicarbonyltris(2,4,6-tri-isopropylbenzenethiolato)molybdate(II) and (methyl cyanide)(phenyldiazenido)tris(2,4,6-tri-isopropylbenzenethiolato)molybdenum(IV) respectively.

Supplementary data available (No. SUP 56331, 14 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. units employed: atm = 101 325 Pa, mmHg ≈ 13.6 × 9.8 Pa.

Table 1. Arenethiolato-complexes of molybdenum and tungsten

		Analysis [a]				U.v.	^{1}H N.m.r.(δ/p.p.m.)
Complex	Colour	C	H	N	ν(CO)[b]/cm^{-1}	λ$_{max.}$[c]/nm	and other data[d]
$[PPh_4][Mo(tipt)_3(CO)_2]$	Pink	69.7 (71.2)	8.0 (7.4)		1 846	501 (1 700), 535(sh)	—
$[PPh_4][Mo(dipt)_3(CO)_2]$	Pink	59.4 (59.5)	6.8 (6.6)		1 848	—	—
$[PPh_4][Mo(bipt)_2(CO)_2]$	Pink	56.9 (56.9)	6.6 (5.2)		1 850	—	—
$[PPh_4][Mo(tmt)_3(CO)_2]$	Pink	67.8 (67.4)	6.7 (6.4)		1 846	497 (1 900), 528(sh)	—
$[PPh_4][Mo(SC_6F_5)_3(CO)_2]$	Pink	48.7 (48.5)	2.1 (1.8)		1 865	499	—
$[PPh_4][W(tipt)_3(CO)_2]$	Brown	65.9 (66.4)	7.3 (6.9)		1 825	—	—
$[PPh_4][W(dipt)_3(CO)_2]$	Brown	64.2 (64.3)	6.4 (6.1)		1 828	—	—
$[PPh_4][W(tmt)_3(CO)_2]$	Brown	60.1 (61.5)	5.2 (5.4)		1 815	449 (2 750), 513 (450), 556(sh)	—
$[PPh_4][Mo(tipt)_3(CO)(CNMe)]$	Purple				1 822	—	δ(CN*Me*) 2.60(s), 3.78(s), ν(NC) 2 100[e]
$[PPh_4][Mo(tipt)_3(CO)(CNBu^t)]$	Purple	72.1 (72.9)	7.5 (7.8)	1.0 (1.1)	1 800[f]	554, 564(sh)[g]	δ(CNC*Me*$_3$) 0.41(s) ν(NC) 2 100[e]
$[PPh_4][Mo(tipt)_3(CO)(PMe_2Ph)]$	Purple	71.9 (71.7)	7.4 (7.7)		1 808[f]	561, 564(sh)[g]	δ(^{31}P) 71(s)
$[PPh_4][Mo(tipt)_3(CO)(NCMe)]$	Blue	71.7 (72.4)	7.4 (7.7)	0.8 (1.2)	1 770[f]	—	—
$[PPh_4][Mo(tipt)_3(CO)(NCEt)]$	Blue	70.8 (71.6)	7.5 (7.7)	1.1 (1.1)	1 766[f]	—	—
$[PPh_4][Mo(tipt)_3(CO)(NCBu^t)]$	Blue	69.6 (71.9)	7.3 (7.8)	1.0 (1.1)	1 789[f]	540, 514(sh)[g]	δ(NC*Me*$_3$) 0.46(s)
$[PPh_4][Mo(bipt)_3(CO)(NCMe)]$	Blue	56.8 (57.3)	5.0 (5.4)	1.0 (1.1)	1 775[f]	—	—
$[PPh_4][Mo(SC_6F_5)_3(CO)(NCEt)]$	Purple	49.6 (50.1)	2.4 (2.3)	0.8 (1.3)	1 840[f]	545, 555(sh)[g]	δ(NCC*H*$_2$CH$_3$) 2.05(m); δ(NCCH$_2$C*H*$_3$) 1.14(m)
$[Mo(NNPh)(tipt)_3(NCMe)]$	Green	66.8 (67.2)	8.0 (8.1)	3.8 (4.4)	—	—	ν(NN) 1 573, 1 645 ν(^{15}N^{15}N) 1 565, 1 630

[a] Calculated values in parentheses. [b] In CH_2Cl_2 solution unless otherwise indicated. [c] In MeCN solution, ε(dm^3 mol^{-1} cm^{-1}) in parentheses. [d] ^{1}H N.m.r. in CD_2Cl_2 solution; i.r. as Nujol mulls unless otherwise indicated, s = singlet, m = multiplet. [e] In CH_2Cl_2. [f] Nujol mull. [g] In toluene solution.

colourising. The molybdenum dicarbonyls are pink and those of tungsten brown.

Their i.r. spectra show a single absorption due ν(C–O) consistent with a *trans* arrangement of the two carbonyl ligands. The ν(C–O) values are relatively low, in the ranges 1 846—1 850 cm^{-1} (Mo) and 1 815—1 828 cm^{-1} (W). The exception is $[Mo(SC_6F_5)_3(CO)_2]^-$ where ν(C–O) is shifted to higher frequency at 1 865 cm^{-1} reflecting the electron-withdrawing character of the C_6F_5 groups. However the C_6F_5S complex has a very similar u.v. spectrum to the bulky arenethiolate derivatives.

The ^{1}H n.m.r. spectra of the complexes exhibit the resonances expected for the counter ion and ligand alkyl and arene resonances. The spectrum of $[Mo(tipt)_3(CO)_2]^-$ shows two very broad multiplets attributable to the methine protons of the Pr^i groups. This is consistent with the asymmetric distribution of the bulky arene groups found in the solid-state structure below, and suggests that such a structure is maintained in solution. The ^{15}N n.m.r. spectrum of $[Mo(NNPh)(tipt)_3(NCMe)]$ discussed below is also consistent with the asymmetric solution structure. The tmt complex $[Mo(tmt)_3(CO)_2]^-$ shows only two singlet resonances (ratio 2:1) assigned to the 2,6- and 4-methyl substituents, consistent with a symmetric disposition of the smaller arene groups or perhaps fluxional behaviour. The temperature dependence was not studied.

Structure of $[PPh_4][Mo(tipt)_3(CO)_2]$.—Crystals of $[PPh_4][Mo(tipt)_3(CO)_2]$ suitable for an *X*-ray structure determination were grown from the reaction mixture by slow addition of a solution of $[PPh_4]Br$ in methanol without stirring. An ORTEP representation of the stucture is shown in Figure 2. Atomic co-ordinates are listed in Table 2 and selected bond lengths and angles in Table 3. The tungsten complex $[W(tipt)_3(CO)_2]^-$ has been shown to be isostructural.[8]

The geometry about the molybdenum atom is essentially trigonal bipyramidal with equatorial thiolate ligands and axial carbonyl ligands. The C–Mo–C and Mo–C–O angles are close to 180°; Mo–C(2) [1.99(2)Å] is significantly longer than Mo–C(1) [1.92(2)Å] despite the greater steric crowding about the latter. This difference may be due to repulsion between the C(2)–O(2) ligand, π electrons, and the lone pairs on S(1) and S(3).

The orientation of the thiolate arene substituents, with one above the equatorial plane and two below, contrasts with the situation found in the structures of $[Mo(SPh)_4(NO)]^-$[4] and $[Re(SPh)_3(MeCN)(PPh_3)]$[9] where the equatorial thiolate phenyl groups are orientated towards the NO and MeCN groups respectively. The asymmetric disposition of the bulky arene groups observed here provides a mechanism for reduction of steric crowding. A similar arrangement is found in the structures of $[Ru(tipt)_4(MeCN)]$[5] and $[Re(dipt)_4(NO)]$.[10] The

Table 2. Atom co-ordinates (× 10^4) for $[PPh_4][Mo(tipt)_3(CO)_2]$

Atom	*x*	*y*	*z*
Mo	1 678(1)	2 491(1)	2 250(1)
C(1)	3 198(16)	2 810(13)	2 415(8)
O(1)	4 150(10)	3 017(10)	2 510(6)
C(2)	97(12)	2 096(10)	2 090(7)
O(2)	−833(8)	1 830(8)	1 991(6)
S(1)	1 581(3)	1 937(3)	1 091(2)
S(2)	1 936(3)	4 192(3)	2 528(2)
S(3)	1 384(3)	1 497(3)	3 137(2)
C(11)	2 948(9)	1 110(10)	531(6)
C(12)	3 886(10)	1 152(11)	252(7)
C(13)	4 708(10)	2 070(11)	205(6)
C(14)	4 544(10)	2 948(11)	433(6)
C(15)	3 642(10)	2 945(10)	709(7)
C(16)	2 822(9)	2 015(10)	772(6)
C(1a)	1 649(16)	−508(16)	−135(10)
C(1b)	2 088(11)	93(10)	550(7)
C(1c)	2 447(15)	−529(15)	955(10)
C(1d)	6 734(10)	2 831(10)	313(7)
C(1e)	5 728(9)	2 114(10)	−105(6)
C(1f)	5 673(10)	2 308(10)	−834(7)
C(1g)	3 124(12)	4 321(12)	314(8)
C(1h)	3 503(10)	3 964(10)	923(7)
C(1i)	4 520(11)	4 801(11)	1 299(8)
C(21)	280(11)	4 534(11)	1 847(8)
C(22)	−702(13)	4 721(13)	1 805(10)
C(23)	−1 183(13)	4 782(13)	2 381(10)
C(24)	−723(12)	4 725(12)	2 997(8)
C(25)	210(12)	4 499(12)	3 060(8)
C(26)	708(10)	4 416(10)	2 469(7)
C(2a)	1 288(15)	5 589(14)	1 049(10)
C(2b)	759(11)	4 484(11)	1 197(8)
C(2c)	14(13)	3 768(13)	616(9)
C(2d)	−3 051(20)	4 337(19)	2 654(13)
C(2e)	−2 326(19)	4 988(20)	2 311(13)
C(2f)	−2 169(24)	5 887(23)	2 116(16)
C(2g)	−132(17)	3 897(17)	4 199(11)
C(2h)	682(13)	4 417(13)	3 759(8)
C(2i)	1 417(16)	5 451(15)	4 063(11)
C(31)	2 874(11)	661(11)	3 514(7)
C(32)	3 840(12)	700(12)	3 878(8)
C(33)	4 448(11)	1 544(12)	4 332(7)
C(34)	4 143(11)	2 341(12)	4 442(8)
C(35)	3 191(11)	2 355(11)	4 092(7)
C(36)	2 593(10)	1 508(10)	3 609(7)
C(3a)	2 774(16)	−919(15)	2 753(11)
C(3b)	2 174(11)	−289(11)	3 025(8)
C(3c)	1 275(14)	−977(14)	3 356(10)
C(3d)	6 467(14)	2 448(14)	4 542(10)
C(3e)	5 528(12)	1 560(14)	4 724(9)
C(3f)	5 440(14)	1 605(14)	5 479(9)
C(3g)	2 453(14)	3 228(15)	4 946(9)
C(3h)	2 862(12)	3 229(12)	4 276(8)
C(3i)	3 781(14)	4 218(14)	4 229(10)
P	2 939(3)	767(3)	7 260(2)
C(111)	3 940(8)	−610(8)	7 152(4)
C(112)	4 428(8)	−1 232(8)	7 410(4)
C(113)	4 456(8)	−1 332(8)	8 102(4)
C(114)	3 995(8)	−809(8)	8 534(4)
C(115)	3 507(8)	−187(8)	8 276(4)
C(116)	3 479(8)	−87(8)	7 584(4)
C(121)	1 038(8)	602(7)	7 773(4)
C(122)	451(8)	805(7)	8 282(4)
C(123)	977(8)	1 495(7)	8 865(4)
C(124)	2 038(8)	1 984(7)	8 988(4)
C(125)	2 678(8)	1 781(7)	8 428(4)
C(126)	2 152(8)	1 091(7)	7 846(4)
C(131)	5 068(8)	2 036(7)	7 306(4)
C(132)	5 875(8)	2 954(7)	7 235(4)
C(133)	5 607(8)	3 747(7)	7 026(4)
C(134)	4 532(8)	3 622(7)	6 888(4)
C(135)	3 725(8)	2 705(7)	6 959(4)
C(136)	3 993(8)	1 912(7)	7 168(4)
C(141)	2 417(7)	695(6)	5 878(6)
C(142)	1 801(7)	233(6)	5 254(6)
C(143)	979(7)	−719(6)	5 205(6)
C(144)	773(7)	−1 208(6)	5 781(6)
C(145)	1 390(7)	−746(6)	6 406(6)
C(146)	2 212(7)	206(6)	6 454(6)

Table 3. Selected bond lengths (Å) and angles (°) for $[Mo(tipt)_3(CO)_2]^-$

Mo–C(1)	1.922(21)	Mo–C(2)	1.987(16)
Mo–S(1)	2.332(4)	Mo–S(2)	2.317(5)
Mo–S(3)	2.342(5)	C(1)–O(1)	1.203(24)
C(2)–O(2)	1.164(19)	S(1)–C(16)	1.797(13)
S(2)–C(26)	1.789(16)	S(3)–C(36)	1.812(15)
C(11)–C(12)	1.397(19)	C(11)–C(16)	1.398(21)
C(11)–C(16)	1.500(17)	C(12)–C(13)	1.393(17)
C(13)–C(14)	1.382(22)	C(13)–C(1e)	1.527(19)
C(14)–C(15)	1.365(20)	C(15)–C(16)	1.411(16)
C(15)–C(1h)	1.547(21)	C(1a)–C(1b)	1.485(22)
C(1b)–C(3c)	1.437(28)	C(1d)–C(1e)	1.483(15)
C(1e)–C(1f)	1.504(19)	C(1g)–C(1h)	1.487(23)
C(1h)–C(1i)	1.531(16)		
C(1)–Mo–C(2)	177.3(7)	C(1)–Mo–S(1)	93.8(5)
C(2)–Mo–S(1)	86.2(4)	C(1)–Mo–S(2)	90.5(6)
C(2)–Mo–S(2)	91.9(5)	S(1)–Mo–S(2)	115.3(2)
C(1)–Mo–S(3)	90.7(5)	C(2)–Mo–S(3)	87.1(4)
S(1)–Mo–S(3)	127.4(2)	S(2)–Mo–S(3)	117.0(2)
Mo–C(1)–O(1)	179.0(13)	Mo–C(2)–O(2)	177.7(13)
Mo–S(1)–C(16)	116.4(4)	Mo–S(2)–C(26)	112.8(4)
Mo–S(3)–C(36)	114.7(5)		

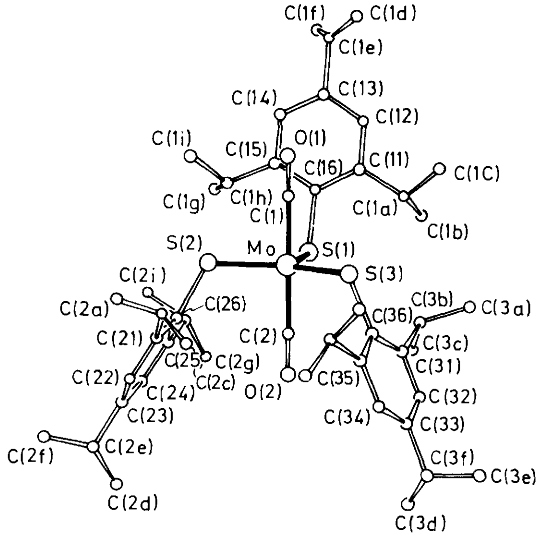
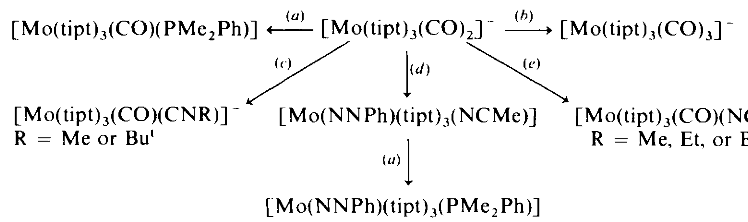


Figure 2. An ORTEP view of the structure of $[Mo(tipt)_3(CO)_2]^-$

Mo–S–C angles lie in the range 112.8(4)—116.4(4)° and are similar to those found in related trigonal-bipyramidal arenethiolate complexes and somewhat wider than those encountered in other arenethiolato-complexes with different geometries. This may be due to steric distortion but could also be due to the thiolate sulphurs acting as weak π-donors. This would also serve to explain the relatively short Mo–S distances [mean 2.331(5)Å] compared with *ca.* 2.40 Å in $[MoO(SPh)_4]^-$ [11] and



Scheme. Substitution reactions of $[Mo(tipt)_3(CO)_2]^-$: (*a*) PMe_2Ph, toluene, room temperature (r.t.); (*b*) CO, 1 atm, CH_2Cl_2, r.t.; (*c*) RNC, toluene, r.t.; (*d*) $[N_2Ph][BF_4]$, MeCN, r.t.; (*e*) RCN, toluene, reflux

2.44 Å in $[Mo_2O_4(SPh)_4]^{2-}$.[12] Also the S–C vectors lie approximately parallel to the OC–Mo–CO axis rather than in the equatorial plane. The latter arrangement would minimise steric interactions but the observed orientation facilitates maximum Mo–S π-interaction within the equatorial plane.

There are no remarkable features of the structure of the $[PPh_4]^+$ cation, where the phenyl rings were refined as rigid groups. There are no particular contact distances between cation and anion so the steric forces responsible for the arenethiolate disposition are intramolecular. This is also supported by the observation of analogous structures for neutral trigonal-bipyramidal complexes of the arenethiolates.[5,10]

Reactivity of $[PPh_4][M(tipt)_3(CO)_2]$ (M = Mo *or* W).—The anions $[M(tipt)_3(CO)_2]^-$ (M = Mo or W) have a formal count of 14 valence electrons and this coupled with their five-co-ordination might be expected to lead to facile addition and substitution chemistry. Both types of reaction are in fact found and the chemistry of the anions is summarised in the Scheme.

A third CO molecule is readily bound when solutions of the dicarbonyl anions are exposed to 1 atm of CO. This is accompanied by a colour change from pink to orange-brown (M = Mo) or to a more intense brown colour (M = W). The reaction of $[W(dipt)_3(CO)_2]^-$ with CO was monitored by i.r. spectroscopy in dichloromethane solution. The single ν(CO) band at 1 828 cm^{-1} in the dicarbonyl is immediately replaced by three bands at 1 945, 1 875, and 1 828 cm^{-1} on addition of CO. The band at 1 828 cm^{-1} is not due to residual starting material as ^1H n.m.r. and u.v. spectroscopy show that there is no $[W(dipt)_3(CO)_2]^-$ present. The observation of three bands assignable to ν(C–O) is consistent with meridional rather than facial geometry. The dicarbonyl anion is readily regenerated by purging the solution briefly with dinitrogen. Although as evidenced by colour changes the anions $[M(tipt)_3(CO)_2]^-$ react rapidly with acetylene, no characterisable products could be isolated.

Under the reaction conditions delineated in the Scheme $[Mo(tipt)_3(CO)_2]^-$ reacts with a variety of small molecules to give the blue to purple species $[Mo(tipt)_3(CO)L]^-$ (L = MeCN, EtCN, BuᵗCN, PMe_2Ph, MeNC, or BuᵗNC). Selected spectroscopic and analytical data for these complexes are summarised in Table 1. The general similarity of their spectra to the parent dicarbonyl anion suggests that they have analogous structures. However all these complexes are very much more air-sensitive than the dicarbonyl species and bleach extremely rapidly on exposure to air even as solids.

All the complexes $[Mo(tipt)_3(CO)L]^-$ show a single i.r. band assignable to ν(C–O) at lower frequency than that for the parent dicarbonyl anion. The lowest values are shown for L = cyanide where the CO ligand lies *trans* to relatively weak π-acceptor ligands. The isocyanide complex $[Mo(tipt)_3(CO)(CNMe)]^-$ exists as two isomers in solution as evidenced by two single ^1H n.m.r. resonances assignable to the isocyanide methyl group. Thus isomers may arise from the asymmetric orientation of the arenethiolate groups discussed above, with one having one isocyanide lying between two arene rings and the other adjacent to one. A similar isomerisation is found for the complex $[Re(tipt)_3(CO)(NCMe)]$, to be described elsewhere.[13]

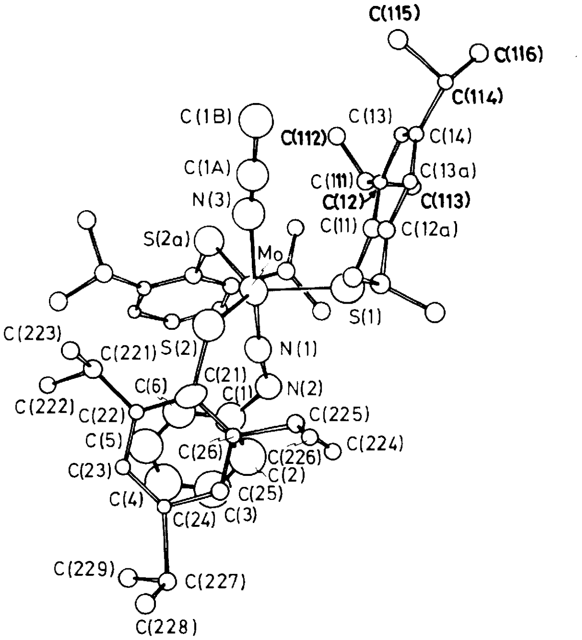


Figure 3. An ORTEP view of the structure of $[Mo(NNPh)(tipt)_3(NCMe)]$ (some isopropyl groups omitted for clarity)

The Scheme also outlines the reaction of $[Mo(tipt)_3(CO)_2]^-$ with a benzenediazonium salt in MeCN. This reaction occurs smoothly at room temperature with evolution of carbon monoxide and formation of the bright green diazenido-complex $[Mo(NNPh)(tipt)_3(NCMe)]$. This complex is a non-electrolyte, is moderately air-stable in the solid state and in solution, and can be readily recrystallised from hot MeCN.

The ^1H n.m.r. spectrum shows the arene proton resonances expected for the diazenide ligand and arenethiolate groups, a singlet for the MeCN protons, and complex multiplets for the thiolate alkyl substituents. Two strong absorptions in the i.r. spectrum at 1 573 and 1 645 cm^{-1} appeared to be associated with the N–N group of the diazenido-ligand. This assignment was confirmed by ^{15}N-labelling of the β-nitrogen which shifts both bands in this region, indicating strong coupling between the N–N stretching and phenyl ring vibrations. The isotope effect is comparable in magnitude and direction with that found for $[Ru(NNPh)(CO)(PPh_3)_2][PF_6]$.[19] Since the Ru complex has a 'singly-bent' diazenido-ligand this suggests a similar geometry for the molybdenum complex. This was confirmed by an *X*-ray crystal-structure determination of $[Mo(NNPh)(tipt)_3(NCMe)]$.

Structure of $[Mo(NNPh)(tipt)_3(NCMe)]$.—Suitable dark green crystals for the *X*-ray study were obtained from hot

Table 4. Atom co-ordinates (× 10^4) for [Mo(NNPh)(tipt)$_3$(NCMe)]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	5 804(2)	2 500	4 916(1)	C(116)	1 947(45)	2 887(19)	7 537(13)
S(1)	6 668(5)	2 500	5 706(2)	C(21)	6 410(8)	1 151(4)	4 225(3)
S(2)	5 113(3)	1 539(2)	4 587(1)	C(22)	6 310(8)	1 132(4)	3 722(3)
N(1)	7 556(12)	2 500	4 706(4)	C(23)	7 312(8)	810(4)	3 452(3)
N(2)	8 796(13)	2 500	4 629(5)	C(24)	8 415(8)	507(4)	3 684(3)
N(3)	3 622(14)	2 500	5 186(4)	C(25)	8 516(8)	525(4)	4 187(3)
C(1)	9 403(18)	2 500	4 165(5)	C(26)	7 514(8)	847(4)	4 458(3)
C(2)	10 853(26)	2 500	4 138(8)	C(221)	5 071(20)	1 423(8)	3 492(7)
C(3)	11 488(26)	2 500	3 687(8)	C(222)	5 409(24)	1 674(11)	2 958(7)
C(4)	10 767(22)	2 500	3 287(7)	C(223)	3 835(20)	984(10)	3 498(7)
C(5)	9 399(23)	2 500	3 306(8)	C(224)	7 261(17)	149(8)	5 183(5)
C(6)	8 681(20)	2 500	3 760(6)	C(225)	7 687(18)	790(8)	5 014(5)
C(11)	5 245(16)	2 500	6 130(5)	C(226)	9 100(19)	961(10)	5 186(6)
C(12)	4 727(12)	1 925(6)	6 297(4)	C(227)	9 942(32)	57(15)	3 519(11)
C(13)	3 654(13)	1 926(6)	6 644(4)	C(228)	10 151(41)	534(20)	3 046(12)
C(14)	3 108(19)	2 500	6 813(6)	C(229)	9 463(32)	− 504(15)	3 374(11)
C(111)	5 336(17)	1 293(8)	6 128(5)	C(227′)	9 195(37)	177(16)	3 293(11)
C(112)	4 233(21)	801(9)	5 989(7)	C(228′)	10 521(43)	404(21)	3 300(13)
C(113)	6 237(25)	1 026(12)	6 482(9)	C(229′)	8 659(43)	− 139(20)	2 925(15)
C(114)	1 920(36)	2 500	7 203(12)	C(1A)	2 618(18)	2 500	5 363(6)
C(115)	1 194(55)	2 135(22)	7 102(17)	C(2A)	1 195(20)	2 500	5 598(9)

There is a crystallographically imposed plane of symmetry passing through the atoms C(1), C(2), C(3), C(4), C(5), C(6), N(1), N(2), Mo, S(1), C(11), and C(14). Primed atoms are related to the unprimed ones by this plane.

Table 5. Selected bond lengths (Å) and angles (°) for [Mo(NNPh)-(tipt)$_3$(NCMe)]

Mo–S(1)	2.336(4)	S(2)–C(21)	1.794(9)
Mo–S(2)	2.312(3)	S(1)–C(11)	1.802(15)
Mo–S(2a)	2.312(3)	N(2)–C(1)	1.409(20)
Mo–N(1)	1.782(12)	N(1)–N(2)	1.211(17)
Mo–N(3)	2.227(14)	N(3)–C(1)	1.082(22)
S(1)–Mo–S(2)	118.1(1)	S(1)–Mo–N(3)	91.3(3)
S(1)–Mo–N(1)	88.2(4)	N(1)–Mo–N(3)	179.4(5)
S(2)–Mo–N(1)	98.3(2)	S(2)–Mo–S(2a)	121.6(2)
S(1)–Mo–S(2a)	118.1(1)	N(3)–Mo–S(2a)	82.0(2)
N(1)–Mo–S(2a)	98.3(2)	Mo–S(2)–C(21)	114.6(3)
Mo–S(1)–C(11)	109.7(5)	N(1)–N(2)–C(1)	124.7(13)
Mo–N(1)–N(2)	171.2(11)	N(2)–C(1)–C(2)	117.5(15)
Mo–N(3)–C(1)	172.7(13)		

MeCN. An ORTEP representation of the structure is given in Figure 3. Atomic co-ordinates are given in Table 4 and selected bond lengths and angles in Table 5.

The geometry about the molybdenum atom is directly analogous to the dicarbonyl anion precursor with equatorial thiolate ligands and the NNPh and MeCN ligands occupying axial sites. There is a crystallographically imposed plane of symmetry passing through the atoms C(1), C(2), C(3), C(4), C(5), C(6), N(2), N(1), Mo, S(1), C(11), C(14). The phenyl rings of the two symmetry related arene groups were refined as rigid rings.

As expected from the i.r. data, the diazenido-ligand is singly bent, and the Mo–N and N–N distances of 1.782(12) and 1.211(17) Å are very similar to those found in other metal diazenido-complexes.[15] The disposition of the thiolate arene groups with respect to the equatorial plane is also analogous to that found in the dicarbonyl. Although ^{15}N n.m.r. suggested two isomers in solution, differing in the orientation of the diazenide ligand relative to the arene thiolate, there is no evidence of disorder of the NNPh ligand in the solid state. The Mo–N distance to the MeCN ligand is somewhat long at 2.227(14) Å, consistent with its facile replacement by other neutral two-electron donors.

Conclusions

This paper describes the first reported examples of monomeric thiolato-carbonyl complexes of molybdenum and tungsten and also their substitution chemistry to yield monomeric isocyanide and cyanide derivatives. The diazenido-complex is the first to contain the NNPh ligand bound to a thiolato-ligated metal ion. The isolation of these complexes utilising bulky *ortho*-substituted arenethiolates supports the initial premise that such ligands should be capable of providing sites which will bind simple π-acceptor molecules. Such species are of interest in understanding the type of metal–sulphur sites that will interact with dinitrogen.

Experimental

Structure Determinations of [Mo(tipt)$_3$(CO)$_2$]$^-$ *and* [Mo-(NNPh)(tipt)$_3$(NCMe)].—The crystal parameters and details of the experimental procedures adopted are summarised in Table 6.

Preparation of Complexes.—All reactions were carried out in dry, oxygen-free solvents, prepared by distillation from appropriate drying agents under dry dinitrogen. Standard Schlenk and glove-box techniques were used throughout. Infrared spectra were recorded on a Pye-Unicam SP2000 i.r. spectrophotometer, electronic spectra on a Perkin-Elmer Lambda 5 u.v.–visible spectrophotometer, and n.m.r. spectra on a JEOL FX90Q spectrometer. Carbon, H, and N analyses were carried out by Mrs. G. Olney, University of Sussex (for air-stable compounds). Air-sensitive compounds were analysed for C, H, and N by Mr. C. Macdonald using a glove-box under dinitrogen. Sulphur, halogen, and phosphorus analyses were carried out by Micro Analysis Limited, or by Butterworth Laboratories. Molecular weights were determined cryoscopically in benzene. 360-MHz ^{1}H n.m.r. and ^{15}N n.m.r. spectra were measured using a Bruker WM350 instrument.

The sterically hindered thiols Htipt, Hdipt, Htmt, and Hbipt were prepared as described below. [MoBr$_2$(CO)$_4$][16] and [WBr$_2$(CO)$_4$][17] were prepared by modifications of literature methods as described below.

Table 6. Summary of crystal and experimental details

	$[Mo(tipt)_3(CO)_2]^-$	$[Mo(NNPh)(tipt)_3(NCMe)]$
(*a*) Crystal parameters[a]		
Space group	$P\bar{1}$	*Pnma*
a/Å	13.451(2)	9.962(2)
b/Å	14.229(2)	21.002(4)
c/Å	19.862(3)	27.646(4)
α/°	96.11(1)	90.0
β/°	94.11(1)	90.0
γ/°	111.04(1)	90.0
U/Å^3	3 502.9(8)	5 583.2(12)
Z	2	4
D_c/g cm^{-3}	1.11	1.13
(*b*) Measurement of intensity data		
Crystal dimensions (mm)	0.25 × 0.17 × 0.30	0.24 × 0.18 × 0.21
Standards	3 collected every 197 reflections, corrected for 11% decomposition	3 collected every 197 reflections, no deviations during collection
No. of reflections collected	4 956	4 658
No. of independent reflections used	2 939 with $I_o > 3\sigma(I_o)$	1 772 with $I_o > 3\sigma(I_o)$
(*c*) Reduction of intensity data and summary of structure solution and refinement[b]		
Absorption coefficient cm^{-1}	3.3	3.68
Final discrepancy factors[c]	R 0.0755 R' 0.0721	0.075 0.080
Goodness of fit[d]	1.52	1.45

Details common to both complexes: diffractometer, Nicolet *R*3*m*; radiation, Mo-K_α (λ = 0.710 69 Å); scan mode, coupled θ (crystal–2θ (counter); variable scan rate, 3—30° min^{-1}; scan range, $2 < 2\theta < 45°$; scan length, from $[2\theta(K_{\alpha 1}) - 1.0]$ to $[2\theta(K_{\alpha 2}) + 1.0]°$; background measurement, stationary counter, stationary crystal at beginning and end of each 2θ scan, each taken for half the time of the scan; absorption correction, not applied; neutral atomic scattering factors used throughout (D. T. Cromer and J. B. Mann, *Acta Crystallogr.*, 1968, **24**, 321); anomalous dispersion applied to all non-hydrogen atoms ('International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3).

Structure solution: Mo atom located from a sharpened Patterson map; all other non-hydrogen atoms were located on subsequent difference Fourier maps. Hydrogen atoms were included as fixed contributors in the final refinement cycles.

[a] From a least-squares fitting of the setting angle of 25 reflections. [b] All calculations were performed on a Data General Nova 3 computer with 32K of 16-bit words using local version of the Nicolet SHELXTL interactive crystallographic software package as described by G. M. Sheldrick, Nicolet SHELXTL Operations Manual, Nicolet XRD Corp., Cupertino, 1979. [c] $R = \Sigma[|F_o| - |F_c|/\Sigma|F_o|]$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = 1/\sigma^2(F_o) + g^*(F_o)^2$; $g = 0.001$. [d] $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$, where N_o is the number of observations and N_v is the number of variables.

Dibromotetracarbonylmolybdenum(II). $[Mo(CO)_6]$ (5 g, 13.5 mmol) was ground to a fine powder and suspended in dichloromethane (40 cm^3). The suspension was cooled to −70 °C in dry-ice–acetone and bromine (2.40 g, 15.0 mmol) was added dropwise. After 1 h at −70 °C the suspension was allowed to warm to room temperature and filtered. Reduction of the volume *in vacuo* gave orange microcrystalline $[MoBr_2(CO)_4]$ which was filtered off, washed with diethyl ether, and dried *in vacuo*. Yield 60—70%.

Dibromotetracarbonyltungsten(II). This complex was prepared similarly to $[MoBr_2(CO)_4]$ from $[W(CO)_6]$ and Br_2.

2,4,6-*Tri-isopropylbenzenethiol* (Htipt). Lithium aluminium hydride (27 g, 0.71 mmol) was suspended in diethyl ether (200 cm^3) in a flask equipped with a condenser and cooled to 0 °C in an ice-bath. While this suspension was rapidly stirred magnetically, a solution of 2,4,6-tri-isopropylbenzenesulphonyl chloride (Aldrich, 100 g, 0.33 mmol) in diethyl ether (300 cm^3) was added dropwise. When this addition was complete and the initial vigorous reaction had subsided a further 13 g (0.34 mol) of lithium aluminium hydride were added and the solution heated under reflux for 5 h. The excess of hydride was then destroyed by dropwise addition of methanol. The mixture was then acidified with 2 mol dm^{-3} H_2SO_4 and extracted with diethyl ether (3 × 200 cm^3). The ether extracts were dried over $MgSO_4$ and the ether removed on a rotary evaporator. The residue was distilled (b.p. 117—120 °C, 0.3 mmHg) to give 74 g (87%) of 2,4,6-tri-isopropylbenzenethiol.

2,4,6-*Trimethylbenzenethiol* (Htmt). This was prepared similarly to Htipt, from 2,4,6-trimethylbenzenesulphonyl chloride (Aldrich) using similar molar ratios of $LiAlH_4$, in similar yield (b.p. 69—72 °C, 0.3 mmHg).

2,6-Di-isopropylbenzenethiol (Hdipt). Crude 2,6-di-isopropylphenol (Aldrich, 100 g, 0.51 mmol) was dissolved in *N*,*N*-dimethylformamide (250 cm^3) and sodium hydride (15.3 g of 80% dispersion in oil, 0.51 mmol) was added slowly. When gas evolution was complete *N*,*N*-dimethylthiocarbamoyl chloride[18] (63 g, 0.51 mmol) was added slowly. On completion of the addition, the solution was heated at 100 °C for 16 h and then cooled and poured into 1.5 l of 2% aqueous KOH. The resulting precipitate was filtered off and recrystallised from hot ethanol to give off-white *O*-2,6-di-isopropylphenyl *N*,*N*-dimethylthiocarbamate (50 g, 34%). This material was stirred and heated at 230 °C for 48 h under dinitrogen. On cooling the solid product, crude *S*-2,6-di-isopropylphenyl *N*,*N*-dimethylthiocarbamate, was used without purification for the next step. The crude material (50 g, 0.19 mol) was dissolved in 1,2-dimethoxyethane (200 cm^3) and the solution added dropwise to a stirred suspension of $LiAlH_4$ (22 g, 0.58 mmol) in 1,2-dimethoxyethane (150 cm^3) cooled in an ice-bath. When the reaction had subsided the solution was heated under reflux for 6 h. Excess hydride was destroyed by addition of methanol. Acidification, ether extraction, drying, and solvent removal were carried out as for Htipt. The final residue was distilled to give 2,6-di-isopropylbenzenethiol as a colourless liquid (20 g, 20% based on 2,6-di-isopropylphenol).

4-*Bromo*-2,6-*di-isopropylbenzenethiol* (Hbipt). Crude 2,6-di-isopropylphenol (100 g, containing 0.51 mmol) was dissolved in glacial acetic acid (200 cm^3). Dibromine (81.6 g, 0.51 mol) was added dropwise to a stirred solution. The mixture was then poured into water (500 cm^3), forming a brown oil which was washed repeatedly with water and dried over $MgSO_4$ to give crude 4-bromo-2,6-di-isopropylphenol (118 g, 91%). This was used without purification to prepare Hbipt in an analogous manner to Hdipt above. Overall yield 15% based on 2,6-di-isopropylphenol (b.p. 140—141 °C, 0.3 mmHg).

Tetraphenylphosphonium Dicarbonyltris(2,4,6-*trimethylbenzenethiolato*)*molybdate*(II), $[PPh_4][Mo(tmt)_3(CO)_2]$. $[MoBr_2(CO)_4]$ (1.28 g, 3.5 mmol) was dissolved in methanol (40 cm^3) and Htmt (1.0 g, 10.8 mmol) added, followed by triethylamine (1.5 cm^3, 10.8 mmol). The solution became orange then pink with slow CO evolution. Addition of excess solid $[PPh_4]Br$ precipitated the complex as a pink microcrystalline solid (1.94 g, 76%).

The following complexes were prepared in a directly analogous fashion from $[MBr_2(CO)_4]$ (M = Mo or W) and the appropriate thiol: $[PPh_4][M(SR)_3(CO)_2]$ (M = Mo, SR = tipt, dipt, bipt, or SC_6F_5; M = W, SR = tmt or dipt). For M = W the crude products may be contaminated with $[W(SR)_3(CO)_3]^-$, but this can easily be removed by recrystallisation from dichloromethane–methanol. Yields 60—75%.

Tetraphenylphosphonium Dicarbonyltris(2,4,6-*tri-isopropylbenzenethiolato*)*tungstate*(II), $[PPh_4][W(tipt)_3(CO)_2]$. *Method 1.* Sodium hydride (0.06 g of 80% dispersion in mineral oil, 2.0 mmol) was suspended in thf (20 cm^3) and Htipt (0.47 g, 2.0 mmol) added. After stirring for 0.5 h the flask was purged with CO and $[WCl_4(thf)_2]$ (0.2 g, 0.43 mmol) added to give a brown solution after 0.5 h. The solvent was removed *in vacuo* and the residue extracted into methanol. The brown solution was filtered and addition of $[PPh_4]Br$ gave the complex (0.28 g, 62%).

Method 2. As above starting from $[WBr_2(CO)_4]$.

Tetraphenylphosphonium Carbonyl(*t-butyl isocyanide*) tris(2,4,6-*tri-isopropylbenzenethiolato*)*molybdate*(II), $[PPh_4][Mo(tipt)_3(CO)(CNBu^t)]$. To a suspension of $[PPh_4][Mo(tipt)_3(CO)_2]$ (0.35 g, 0.29 mmol) in toluene (30 cm^3) was added 1 cm^3 of a solution of Bu^tNC in toluene (6% by volume) (0.58 mmol). The solution was stirred for 3 h and filtered. The volume was reduced *in vacuo* to *ca.* 15 cm^3, whereupon purple crystals formed which were collected, washed with pentane, and dried *in vacuo*. Yield 64%.

Tetraphenylphosphonium Carbonyl(*methyl isocyanide*)*tris*(2,4,6-*tri-isopropylbenzenethiolato*)*molybdate*(II), $[PPh_4][Mo(tipt)_3(CO)(CNMe)]$. To a suspension of $[PPh_4][Mo(tipt)_3(CO)_2]$ (0.35 g, 0.29 mmol) in toluene (20 cm^3) was added a solution of MeNC (0.02 g, 0.5 mmol) in toluene (10 cm^3). After stirring for 6 h a small amount of purple precipitate had formed, which was collected and washed with pentane. The solid was impure and not suitable for microanalysis. Other products formed in this reaction were not characterised.

Tetraphenylphosphonium Carbonyl(*dimethylphenylphosphine*)*tris*(2,4,6-*tri-isopropylbenzenethiolato*)*molybdate*(II), $[PPh_4][Mo(tipt)_3(CO)(PMe_2Ph)]$. To a suspension of $[PPh_4][Mo(tipt)_3(CO)_2]$ (0.5 g) in toluene (30 cm^3) was added an excess of PMe_2Ph (*ca.* 0.5 cm^3). The solution was heated to reflux for 2 h, cooled to room temperature, and filtered. The solvent was removed *in vacuo*, and the residue stirred with methanol (10 cm^3) to give microcrystals which were collected and washed with pentane. Yield 67%.

Tetraphenylphosphonium Carbonyl(*methyl cyanide*)*tris*(2,4,6-*tri-isopropylbenzenethiolato*)*molybdate*(II), $[PPh_4][Mo(tipt)_3(CO)(NCMe)]$. A solution of $[PPh_4][Mo(tipt)_3(CO)_2]$ in MeCN was heated to reflux for 8 h. The resulting deep blue solution was evaporated to dryness and the residue recrystallised from toluene, collected and washed with pentane. Yield 58%.

$[PPh_4][Mo(bipt)_3(CO)(NCMe)]$ was prepared analogously from $[PPh_4][Mo(bipt)_3(CO)_2]$. The complexes $[PPh_4][Mo(tipt)_3(CO)(NCEt)]$ and $[PPh_4][Mo(tipt)_3(CO)(NCBu^t)]$ were prepared in the same way using EtCN or Bu^tCN and reflux times of 4 and 2 h respectively. The complex $[PPh_4][Mo(SC_6F_5)_3(CO)(NCEt)]$ was prepared analogously from $[Mo(SC_6F_5)_3(CO)_2]$; the complex is less soluble in toluene and the extraction step is not complete, however a low yield of the pure crystalline complex can be obtained by this method.

(*Methyl cyanide*)(*phenyldiazenido*)*tris*(2,4,6-*tri-isopropylbenzenethiolato*)*molybdenum*(IV), $[Mo(NNPh)(tipt)_3(NCMe)]$. To a solution of $[PPh_4][Mo(tipt)_3(CO)_2]$ (0.39 g, 0.33 mmol) in MeCN was added a MeCN solution of $[N_2Ph][BF_4]$ (0.063 g, 0.33 mmol in 3 cm^3) dropwise. A green crystalline precipitate was rapidly formed and CO was evolved. The solid was collected, washed with MeCN, and dried *in vacuo*. Crystals suitable for *X*-ray studies were grown by slow cooling of a hot MeCN solution. The $^{14}N^{15}NPh$ analogue was prepared similarly from $[^{14}N^{15}NPh][BF_4]$.

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