Co-ordination Chemistry of 2,6-Diphenylthiophenol. The Syntheses and X-Ray Crystal Structures of Some Molybdenum and Rhodium Complexes with σ- or η^6-Phenyl–Metal Interactions†

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Reaction of $[MoCl_2(CO)_4]$ with the 2,6-diphenylthiophenolate anion (dpt) gives the complex $[Mo(\eta^6\text{-}dpt)(dpt)(CO)]$, with one thiol phenyl substituent η^6-bonded to the molybdenum. Crystal data: space group $P2_1/c$ with $a = 13.939(3)$, $b = 10.548(3)$, $c = 20.863(5)$ Å, $\beta = 106.88(1)°$ and $Z = 4$. The η^6-arene ligand is labile and is reversibly replaced by CO. Replacement of this ligand also occurs with 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), and 1,2-bis(diphenylphosphino)ethane (dppe) to give the dicarbonyl complexes $[Mo(dpt)_2(CO)_2L]$ (L = bipy or phen) or the monocarbonyl complex $[Mo(dpt)_2(CO)(dppe)]$. The X-ray crystal structure of the bipy derivative and the mechanism of its formation is discussed. Crystal data: space group $P2_1/c$ with $a = 10.567(3)$, $b = 22.843(5)$, $c = 18.341(3)$ Å, $\beta = 105.2(2)°$ and $Z = 4$. Reaction of $RhCl_3$ with dpt gave the dinuclear species $[Rh_2\{\mu\text{-}SC_6H_3(C_6H_4)\text{-}2\text{-}Ph\text{-}6\}_2(dpt)_2(NCMe)_2]$. An X-ray crystal structure reveals that each bridging thiolate ligand is also σ-bonded to rhodium [Rh–C 2.016(8) Å] *via* one of the phenyl carbons of the thiolate substituents. Crystal data: space group $P2_1/n$, $a = 11.991(2)$, $b = 20.426(4)$, $c = 15.910(4)$ Å, $\beta = 90.42(1)$ and $Z = 2$.

The dominant feature of the co-ordination chemistry of the 2,4,6-triisopropylthiophenol (Htipt) and 2,4,6-trimethylthiophenol (Htmt) ligands is the formation of five-co-ordinate complexes with trigonal-bipyramidal geometries[1–8] in particular for the early and middle transition metals. In the hope of reducing the predilection for this type of five-co-ordination, we have studied the chemistry of the more sterically hindered thiol 2,6-diphenylthiophenol (Hdpt). An additional potential advantage of the phenyl-substituted thiol is the reduction in lipophilicity of any complexes, rendering them easier to isolate than those of tipt or tmt.

Previous work has shown that the tipt anion reacts with $[MoCl_2(CO)_4]$ to form the five-co-ordinate anion $[Mo(tipt)_3(CO)_2]^-$.[2] This paper describes the full details of the analogous reaction with Hdpt to form an η^6-arene complex, briefly described earlier.[9] The reactivity of the η^6-arene complex with a series of C-, O-, N- and P-donor ligands is also discussed.

By contrast, the Hdpt anion is shown to react with $RhCl_3$ to give the binuclear complex $[Rh_2\{\mu\text{-}SC_6H_3(C_6H_4)\text{-}2\text{-}Ph\text{-}6\}_2(SC_6H_3Ph_2\text{-}2,6)_2(NCMe)_2]$ with the bridging thiol also σ-bonded *via* a phenyl substituent.

Results and Discussion

Synthesis of the η^6-arene complex $[Mo(\eta^6\text{-}dpt)(dpt)(CO)]$ **1** is achieved by the reaction of $[MoCl_2(CO)_4]$ with 2 equivalents of the sodium salt of 2,6-diphenylthiophenol in 1,2-dimethoxyethane. Complex **1** is isolated as a green powder by first removing the reaction solvent and then triturating the resulting green oil with hexane. The rhodium(III) complex $[Rh_2\{\mu\text{-}SC_6H_3(C_6H_4)\text{-}2\text{-}Ph\text{-}6\}_2(dpt)_2(NCMe)_2]$ **5** is synthesised by the reaction of rhodium trichloride with 2 mole equivalents of 2,6-diphenylthiophenolate anion in acetonitrile. It is obtained as an air-stable red microcrystalline solid directly from the reaction mixture.

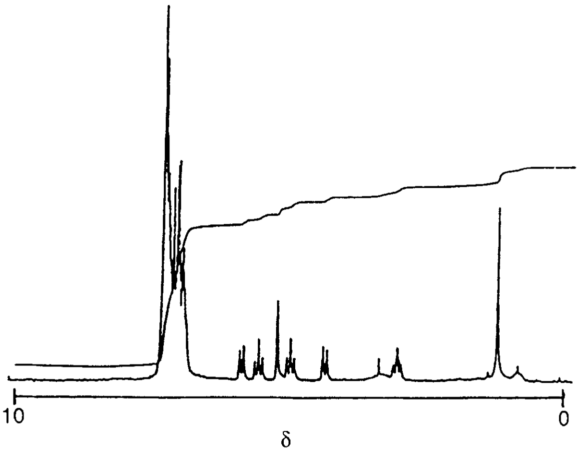

Fig. 1 80 MHz ^1H NMR spectrum ($CDCl_3$) of $[Mo(\eta^6\text{-}dpt)(dpt)(CO)]$ **1**

Spectroscopy.—Table 1 lists analytical and selected spectroscopic data for the complexes of Mo and Rh. Spectroscopic data did not permit an unequivocal assignment of the structure of complex **5**. However, the ^1H NMR data were diagnostic of an η^6-arene interaction in complex **1** with the most striking feature of the NMR spectrum (Fig. 1) being the appearance of five multiplet resonances in the δ 3–6 region, each integrating as one proton. These are assigned to the phenyl protons of an η^6-co-ordinated arene ligand. Complete assignment of the η^6-arene resonances was possible using proton-decoupling procedures (results in Table 1).

The chemical shifts for the η^6-arene ligand lie in the range δ 3–7 and the coupling constants are all 6 Hz. Both parameters

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI units employed: atm = 101 325 Pa, Torr ≈ 133 Pa.

Table 1 Properties of 2,6-diphenylthiophenolate complexes

	Complex	Analysis[a] (%) C	H	N	^{1}H NMR[b]	IR[c] ν(CO)
1	[Mo(η^6-dpt)(dpt)(CO)]	67.9 (68.7)	4.2 (4.0)	— —	3.09 [s, 1, *J*(HH) 7, π] 4.44 [d, 1, *J*(HH) 7, π] 5.06 [s, 1, *J*(HH) 7, π] 5.65 [s, 1, *J*(HH) 7, π] 6.97 [d, 1, *J*(HH) 7, π] 7.1–7.4 (m, 21, aryl)	1930
2	[Mo(dpt)$_2$(CO)$_2$(bipy)]	65.7 (66.4)	3.9 (3.9)	3.2 (3.4)	—	1856 1955
3	[Mo(dpt)$_2$(CO)$_2$(phen)]	69.4 (69.4)	5.3 (5.4)	3.2 (3.2)	7.15–5.45 (m, 26, dpt) 7.75–7.8 (m, 8, phen)	1840 1935
4	[Mo(dpt)$_2$(CO)(dppe)]	71.5 (72.3)	4.7 (5.1)	— —	—	1895
5	[Rh$_2${μ-SC$_6$H$_3$(C$_6$H$_4$)-2-Ph-6}$_2$(dpt)$_2$(NCMe)$_2$]	69.1 (68.4	4.65 (4.35)	2.1 (2.1)	7.35–7.64 (m, aryl)	—

[a] Calculated values in parentheses. [b] Recorded in CDCl$_3$ *vs.* SiMe$_4$ as internal standard. [c] Nujol mulls.

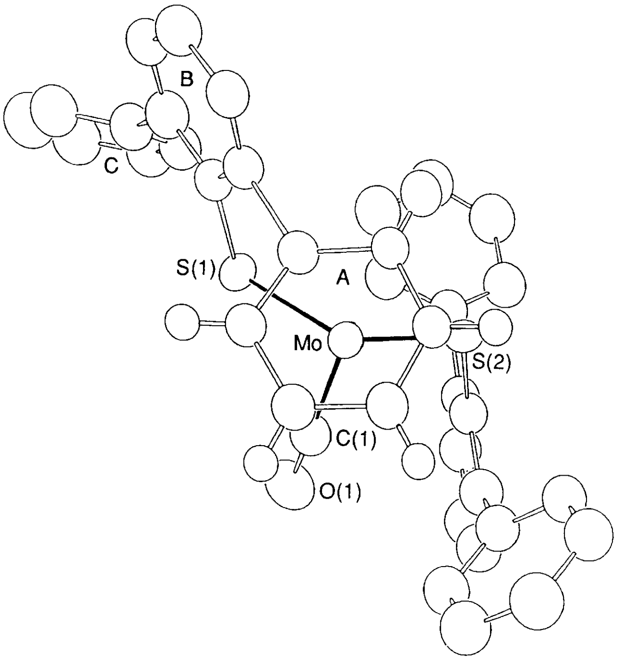


Fig. 2 An ORTEP view of complex **1** showing a partial atom labelling scheme. Bond lengths (Å): Mo–S(1) 2.358(3), M–S(2) 2.329(4), Mo–C(1) 1.978(16), C(1)–O(1) 1.133(19), Mo–C(21) 2.267(12), Mo–C(22) 2.385(13), Mo–C(23) 2.361(12), Mo–C(24) 2.329(11), Mo–C(25) 2.90(11) and Mo–C(26) 2.358(13). Bond angles (°): S(1)–Mo–S(2) 113.1(1), C(1)–Mo–S(1) 85.4(4) and C(11)–C(13)–C(21) 117.9(11)

are of the same order of magnitude as found for other similar η^6-arene complexes.[10,11] Other chelated η^6-arene complexes of Cr and Mo are reported to exhibit at most three resonances. The five proton resonances seen for complex **1** arise from the lower overall symmetry within the molecule. This has been verified by the X-ray crystal structure, discussed in the next section. The *p*-proton resonance for the η^6-arene group is shifted to significantly higher fields than the *o*- and *m*-protons. The ^{1}H NMR spectrum of complex **5** displays a complex multiplet at about δ 7 assigned to the protons in the other phenyl groups of the thiolato-ligand.

The IR spectrum of complex **1** is characterised by a sharp band due to ν(CO) at 1930 cm^{-1}. This value is somewhat higher than those of other monocarbonyl molybdenum(II) complexes.[2,12] The lower ν(CO) values found elsewhere are probably due to either an overall negative charge on the complexes or to the absence of any π-acceptor ligands comparable to the η^6-arene system.

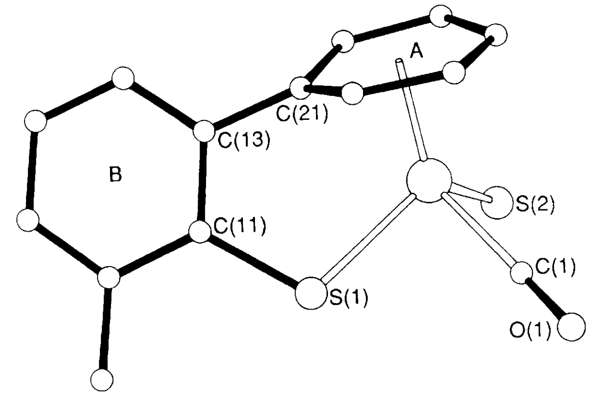


Fig. 3 ORTEP view of complex **1** with the phenyl groups omitted for clarity

X-Ray Crystallography.—Structure of [Mo(η^6-dpt)(dpt)(CO)] **1**. ORTEP views of the molecular structure are shown in Figs. 2 and 3 together with relevant bond lengths and angles. Atomic coordinates are presented in Table 2. The dominant feature of the structure is the presence of a η^6-arene ligand moiety from an *o*-phenyl substituent of one of the thiolate ligands which is also bound *via* sulphur. The overall geometry about Mo is a distorted variant of the 'three-legged piano stool' structure commonly found for mono-η^6-arene complexes.[13]

Steric interactions between the two thiolato-ligands cause an opening of the S(1)–Mo–S(2) angle to 113.1° compared to 85.4 and 89.1° for S(1)–Mo–C(1) and S(2)–Mo–C(1) respectively. There is slight inequivalence in the Mo–S distances, Mo–S(1) 2.358(3) and Mo–S(2) 2.329(4) Å, but both lie within the range found for molybdenum(II) complexes containing 2,4,6-triisopropylthiophenolate ligands.[1,2]

The plane of the non-co-ordinated *o*-phenyl ring, C (Fig. 2), lies at 50.0° to the thiophenol ring, B. η^6-Co-ordination of the *o*-phenyl ring, A, causes an increase of this interplanar angle to 70.8°. The rotation of ring A relative to B accompanies a displacement of the molybdenum atom from the plane of the chelate ring atoms C(21), C(13), C(11) and S(1) (Fig. 3), which also achieves a position on the normal through the centre of ring A. Atom C(21) lies 0.14 Å from the best-fit plane through the remaining five co-ordinated carbon atoms. A similar but smaller distortion was observed in the structure of [Cr{P-

Table 2 Atomic coordinates for [Mo(η^6-dpt)(dpt)(CO)] **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	8 507(1)	1 293(1)	2 307(1)	C(35)	3 112(12)	−63(15)	507(8)
S(1)	6 839(2)	847(3)	1 685(2)	C(36)	3 679(11)	177(14)	1 162(7)
S(2)	9 173(3)	3 043(3)	1 905(2)	C(41)	9 706(10)	2 644(12)	1 260(6)
C(1)	8 884(10)	220(13)	1 640(7)	C(42)	9 244(10)	3 002(12)	602(6)
O(1)	9 067(8)	−409(9)	1 252(5)	C(43)	9 647(11)	2 642(13)	91(7)
C(11)	6 095(8)	1 225(12)	2 220(5)	C(44)	10 498(12)	1 923(14)	234(8)
C(12)	5 023(9)	1 300(13)	1 993(6)	C(45)	10 998(11)	1 601(13)	875(7)
C(13)	6 610(8)	1 444(11)	2 899(5)	C(46)	10 637(10)	1 980(12)	1 408(6)
C(14)	4 541(10)	1 569(11)	2 470(6)	C(51)	11 236(9)	1 589(11)	2 097(6)
C(15)	5 073(10)	1 797(12)	3 133(7)	C(52)	11 495(10)	337(13)	2 242(7)
C(16)	6 090(10)	1 722(11)	3 340(7)	C(53)	12 101(10)	15(15)	2 887(7)
C(21)	7 714(8)	1 285(12)	3 115(5)	C(54)	12 454(11)	927(14)	3 354(8)
C(22)	8 093(9)	27(12)	3 136(6)	C(55)	12 205(10)	2 181(14)	3 211(7)
C(23)	9 120(9)	−179(12)	3 183(6)	C(56)	11 580(10)	2 480(13)	2 588(6)
C(24)	9 768(9)	891(11)	3 297(6)	C(61)	8 285(9)	3 748(13)	396(6)
C(25)	9 421(9)	2 087(11)	3 384(6)	C(62)	8 321(11)	4 971(13)	165(7)
C(26)	8 405(9)	2 317(12)	3 289(6)	C(63)	7 419(11)	5 656(15)	−61(7)
C(31)	4 473(9)	1 017(12)	1 295(6)	C(64)	6 549(12)	5 143(15)	−63(7)
C(32)	4 674(10)	1 601(13)	771(6)	C(65)	6 509(12)	3 932(15)	160(7)
C(33)	4 122(10)	1 354(14)	110(7)	C(66)	7 397(11)	3 256(14)	409(7)
C(34)	3 347(12)	499(14)	0(8)				

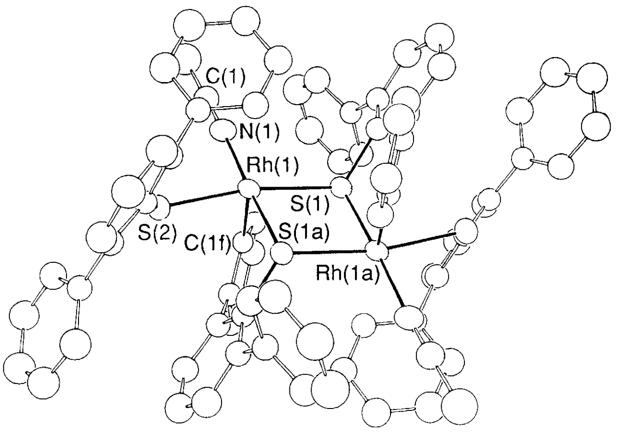


Fig. 4 An ORTEP view of complex **5**. Bond lengths (Å): Rh(1)···Rh(1a) 3.501(1), Rh(1)–S(1) 2.454(2), Rh(1)–S(1a) 2.269(2), Rh(1a)–S(2a) 2.345(3), Rh(1)–N(1) 2.060(8) and Rh(1)–C(1f) 2.016(8). Bond angles (°): S(1)–Rh(1)–S(1a) 80.41(1), S(1)–Rh(1)–C(1f) 86.1(3), S(2)–Rh(1)–S(2a) 94.2(1), S(2)–Rh(1)–N(1) 87.4(2), S(2)–Rh(1)–C(1f) 86.1(3), N(1)–Rh(1)–S(1a) 175.7(2), N(1)–Rh(1)–C(1f) 93.7(3), C(1f)–Rh(1)–S(1a) 90.2 and Rh(1)–S(1)–RhS(1a) 99.6(1)

$(OPh)_2[(CH_2CH_2(\eta^6\text{-}Ph)]\}(CO)_2]$. By contrast, the additional atom in the chelate ring of $[Cr\{PhN{=}C(Ph)CH_2CH_2(\eta^6\text{-}Ph)\}(CO)_2]$[11] apparently allows for more flexibility and permits the η^6-arene ligand to be nearly planar. The Mo–C (η^6-arene) bond distances vary in the range 2.32–2.39 Å and are comparable to those reported for other molybdenum η^6-arene compounds.[10,13]

Structure of $[Rh\{\mu\text{-}SC_6H_3(C_6H_4)\text{-}2\text{-}Ph\text{-}6\}_2(dpt)_2(NCMe)_2]$ **5**. Suitable crystals of complex **5** were grown from the acetonitrile reaction mixture. The molecular structure is shown in Fig. 4 together with relevant bond lengths and angles. Atomic coordinates are given in Table 3. The structure consists of discrete binuclear units possessing a centre of symmetry at the midpoint of the Rh(1)–Rh(1a) vector which imposes planarity upon the Rh_2S_2 moiety. Each Rh atom is five-co-ordinate, displaying square-pyramidal geometry with the two bridging thiolate sulphur atoms S(1) and S(1a), the sulphur of the terminal thiolate ligand S(2), and the nitrogen of the acetonitrile ligand generating the basal plane. The apical ligand is a σ-bonded carbon, arising from an orthometallation reaction of an *o*-phenyl substituent of a bridging thiolate ligand and is part of a six-membered metallacycle ring. An analogous bonding mode has been reported for a 2,6-diphenylphenoxide ligand in a formally five-co-ordinate complex of stoichiometry $[Mo(OR)_3(HNMe_2)]$.[10] Both complexes have M–C bond distances of *ca.* 2.0 Å despite possessing different ligand environments and metal centres.

The four-membered $(Rh\text{-}\mu\text{-}SR)_2$ core has unequal Rh–S bonds with Rh(1)–S(1) and Rh(1a)–S(1) distances of 2.452(2) and 2.269(2) Å respectively. The unusually long Rh(1)–S(1) bond may be due to the geometric constraints imposed by the orthometallation of the thiolato-ligand and the subsequent formation of a ring system comprising Rh–S(1a)–C(11a)–C(12)–C(1a)–C(1f). The six-membered metallacycle has a bite of 90.2(2)° and is noticeably non-planar, which may be a consequence of the strain imposed by the bridging thiolate involved in the chelate ring. This is in contrast to a planar arrangement of the six-membered metallacycle seen in the molybdenum 2,6-diphenylphenoxide complex.[10]

A distinctive feature of complex **5** is that the Rh atoms lie in the basal plane to produce a planar $Rh(\mu\text{-}S)_2S(N)$ moiety. This contrasts to the commonly observed displacement of the metal from the basal plane towards the apical ligand in square-pyramidal complexes such as $[PPh_4][MoO(SCH_2CH_2CH_2S)_2]$ (0.76 Å),[14] $[PPh_4][ReO(SC_6H_2Me_3\text{-}2,4,6)_4]$, (0.71 Å)[15] and $[PPh_4][ReS(SCH_2CH_2S)_2]$ (0.4 Å).[16] The above data support the notion that the magnitude of metal-ion displacement from the basal ligands depends on the nature of the M–L (apical) bond. Thus, small multiply bonded ligands such as the oxo- and sulphido-ligand will give significant displacements, whereas a σ-bonded apical ligand, as in the rhodium dimer system, generates small deviations.

Reactivity of Complex **1**.—(*a*) *With carbon monoxide.* Complex **1** readily reacted with CO at atmospheric pressure in dichloromethane to give a purple solution. The UV–VIS spectra of complex **1** and the purple solution showed intense bands at λ_{max} 465.5 and 506.5 nm (purple solution) respectively with high molar absorption coefficients (ε ≈9000 dm^3 mol^{-1} cm^{-1}). The intensity of these bands suggests that they arise from charge-transfer transitions. The absorption band at *ca.* 700 nm (complex **1**) disappeared when CO was introduced.

Proton NMR experiments demonstrated unequivocally that CO readily displaced the co-ordinated η^6-arene ligand. The high-field resonances characteristic of the η^6-arene ligand disappeared on addition of CO, but reappeared on warming the purple CD_2Cl_2 solution. IR spectroscopy of the purple dichloromethane solution revealed three new strong ν(CO)

Table 3 Atomic coordinates for $[Rh_2\{\mu\text{-}SC_6H_3(C_6H_4)\text{-}2\text{-}Ph\text{-}6\}_2(dpt)_2(NCMe)_2]$ **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	4203(1)	−235(1)	4081(1)	C(25)	1766(9)	−1893(5)	5100(7)
S(1)	4923(2)	732(1)	4822(1)	C(26)	2283(8)	−1484(5)	4537(6)
S(2)	3882(2)	−1214(1)	3349(1)	C(2a)	4240(8)	−2739(5)	3545(6)
N(1)	3312(6)	233(4)	3146(5)	C(2b)	4276(8)	−2615(5)	2683(6)
C(1)	2785(8)	448(5)	2622(7)	C(2c)	5026(9)	−2949(5)	2151(7)
C(2)	2095(10)	728(7)	1952(7)	C(2d)	5727(10)	−3410(6)	2490(7)
C(11)	3985(7)	1329(4)	5214(5)	C(2e)	5708(10)	−3530(6)	3344(7)
C(16)	3755(8)	1869(5)	4695(6)	C(2f)	4985(9)	−3220(5)	3893(7)
C(15)	3047(8)	2356(5)	4976(7)	C(2g)	1863(7)	−816(4)	4402(5)
C(14)	2610(9)	2314(6)	5787(7)	C(2h)	1077(9)	−709(6)	3760(7)
C(13)	7152(8)	−1792(5)	3708(6)	C(2i)	607(11)	−101(6)	3657(8)
C(12)	6525(8)	−1256(5)	3989(6)	C(2j)	870(9)	420(6)	4180(7)
C(1a)	6497(7)	−650(4)	3488(5)	C(2k)	1637(8)	315(5)	4819(7)
C(1b)	7488(8)	−512(5)	3025(6)	C(2l)	2139(8)	−299(5)	4913(6)
C(1c)	7598(10)	36(5)	2556(7)	S(3)	1677(7)	229(4)	−500(5)
C(1d)	6747(8)	486(5)	2524(6)	C(31)	1312(13)	−340(8)	245(9)
C(1e)	5795(8)	378(5)	2986(5)	C(32)	1880(13)	−775(8)	723(10)
C(1f)	5656(7)	−190(4)	3456(5)	C(33)	1294(14)	−1139(8)	1302(10)
C(1g)	4251(8)	1970(5)	3854(6)	C(34)	−138(16)	1069(10)	−1351(11)
C(1h)	5391(8)	2039(5)	3732(6)	C(35)	363(16)	638(9)	−845(11)
C(1i)	5819(9)	2195(5)	2945(7)	C(36)	−214(14)	278(8)	−313(10)
C(1j)	5113(10)	2278(6)	2268(8)	C(3a)	2965(24)	−795(14)	594(17)
C(1k)	3990(11)	2202(6)	2363(8)	C(3b)	3519(27)	−864(14)	−244(19)
C(1l)	3564(9)	2053(5)	3151(7)	C(3c)	4806(26)	−895(15)	−386(19)
C(21)	3170(7)	−1742(4)	4035(5)	C(3d)	5561(26)	−837(14)	310(18)
C(22)	3426(7)	−2410(4)	4100(6)	C(3e)	5161(21)	−863(11)	1147(15)
C(23)	2853(9)	−2802(6)	4680(6)	C(3f)	3991(28)	−782(16)	1224(21)
C(24)	2049(9)	−2535(6)	5191(7)				

Table 4 Atomic coordinates for $[Mo(dpt)_2(CO)_2(bipy)]$, **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	7 344(1)	712(1)	2 052(1)	C(22)	7 252(11)	2 407(6)	4 138(7)
S(1)	8 432(2)	106(1)	1 373(1)	C(23)	7 641(12)	2 141(6)	4 829(7)
S(2)	5 867(2)	1 075(1)	2 704(1)	C(24)	7 513(10)	1 551(5)	4 881(6)
N(1)	5 881(7)	−32(4)	1 789(4)	C(25)	7 948(9)	1 206(4)	4 253(5)
N(2)	5 805(7)	936(4)	988(4)	C(1g)	6 352(10)	2 410(5)	2 747(6)
C(1)	8 557(10)	1 373(5)	2 182(5)	C(1h)	5 095(11)	2 405(5)	2 274(6)
C(2)	8 687(10)	535(4)	2 984(6)	C(1i)	4 801(13)	2 711(5)	1 596(7)
O(1)	9 316(7)	1 745(3)	2 305(4)	C(1j)	5 743(13)	3 021(6)	1 383(7)
O(2)	9 532(7)	493(3)	3 529(4)	C(1k)	7 002(13)	3 036(6)	1 849(7)
C(10)	10 163(9)	97(4)	1 791(5)	C(1l)	7 301(12)	2 744(5)	2 532(7)
C(11)	10 983(10)	512(4)	1 593(6)	C(5g)	6 844(10)	565(4)	4 341(5)
C(12)	12 293(11)	519(4)	1 988(6)	C(5h)	7 938(11)	247(5)	4 688(6)
C(13)	12 806(12)	118(5)	2 546(7)	C(5i)	7 855(12)	−352(6)	4 792(7)
C(14)	12 002(10)	−312(5)	2 718(6)	C(5j)	6 642(13)	−620(7)	4 547(7)
C(15)	10 667(9)	−331(4)	2 339(5)	C(5k)	5 542(13)	−312(6)	4 247(7)
C(1a)	10 562(9)	947(4)	973(5)	C(5l)	5 640(11)	296(5)	4 151(6)
C(1b)	9 832(9)	776(5)	264(5)	C(30)	6 003(12)	−513(5)	2 218(7)
C(1c)	9 573(11)	1 165(5)	−331(7)	C(31)	5 090(13)	−976(6)	2 025(8)
C(1d)	10 022(12)	1 727(6)	−240(7)	C(32)	4 106(14)	−900(7)	1 410(8)
C(1e)	10 753(12)	1 902(6)	455(7)	C(33)	3 927(13)	−428(6)	965(7)
C(1f)	11 016(11)	1 514(5)	1 069(6)	C(34)	4 851(10)	38(5)	1 174(6)
C(5a)	9 898(9)	−817(4)	2 542(5)	C(40)	5 803(11)	1 450(5)	647(6)
C(5b)	9 909(10)	−901(5)	3 303(6)	C(41)	4 769(13)	1 631(6)	42(7)
C(5c)	9 253(12)	−1 378(5)	3 493(8)	C(42)	3 746(14)	1 262(7)	−155(8)
C(5d)	8 632(12)	−1 769(6)	2 975(7)	C(43)	3 698(12)	747(6)	165(7)
C(5e)	8 593(12)	−1 692(6)	2 224(7)	C(44)	4 762(10)	567(4)	756(6)
C(5f)	9 233(10)	−1 209(5)	2 017(6)	Cl(1)	1 050(5)	1 816(2)	4 275(3)
C(20)	6 579(9)	1 495(4)	3 531(5)	Cl(2)	3 467(4)	1 813(2)	3 822(3)
C(21)	6 700(10)	2 097(5)	3 473(6)	C(3)	1 915(13)	1 511(6)	3 692(8)

absorptions at 1950, 1985 and 2085 cm^{-1} and also a weak band at 1925 cm^{-1} which indicated the presence of some η^6-arene starting material.

Isolation of the purple polycarbonyl species was achieved by carrying out the reaction in hexane which yielded a dark purple precipitate, with an identical solution (CH_2Cl_2) IR spectrum to that observed previously when samples were taken from the above purple solution. Unfortunately, microanalytical data were not reproducible, mainly due to ready loss of CO from the isolated purple product even in the solid state. However, the evolution of 3 mol CO from the purple product after exhaustive oxidation with excess of Br_2 suggested that the purple polycarbonyl species contains three carbonyl groups per molybdenum.

(*b*) *Bidentate neutral ligands.* Here it was hoped that a bidentate four-electron donor ligand would displace the η^6-

Table 5 Experimental details for X-ray diffraction study of [Mo(η^6-dpt)(dpt)(CO)] **1**, [Mo(dpt)$_2$(CO)$_2$(bipy)] **2** and [Rh$_2${μ-SC$_6$H$_3$(C$_6$H$_4$)-2-Ph-6}$_2$] **5**

(*a*) Crystal parameters at 23 °C	**1**	**2**	**5**
a/Å	13.939(3)	10.567(2)	11.991(2)
b/Å	10.548(3)	22.843(3)	20.426(2)
c/Å	20.863(5)	18.341(3)	15.910(3)
α/°	90.0	90.0	90.0
β/°	106.88(1)	105.2(2)	90.42
γ/°	90.0	90.0	90.0
U/Å^3	2935(1)	4273.91(15)	3896.7(15)
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
Z	4	4	2
D_c/g cm^{-3}	1.46	1.29	1.14
F(000)	1320	1704	1360
(*b*) Measurement of intensity data[a]			
Scan range/°	$1.0 \leqslant 2\theta \leqslant 45$	$0 < 2\theta \leqslant 45$	$0 < 2\theta \leqslant 45$
Standard reflections	3 every 200	3 every 197	3 every 197
Number of reflections collected	4220	6282	5646
Number of independent reflections used in solution [$I_o > 3\sigma(I_o)$]	1612	2788	3379
(*c*) Reduction of intensity data and summary of structure solution and refinement[b]			
μ/cm^{-1}	5.76	4.4	5.5
Final discrepancy factors R,R'	0.056, 0.052	0.056, 0.059	0.0665, 0.072
Goodness of fit	1.21	1.12	1.59

[a] Details in common: Nicolet R3m diffractometer; Mo-Kα radiation (λ = 0.710 73 Å); scan mode θ–2θ; scan rate 7–30° min^{-1}; scan length from 2θ(Kα1) − 1.0 to 2θ(Kα2) + 1.0°; background measurement, stationary crystal, stationary counter, at the beginning and end of each 2θ scan, each for the time taken for the scan. [b] Details in common: data corrected for background, attenuators, Lorentz and polarisation effects in the usual manner; no absorption correction; Patterson synthesis yielded the metal position, all remaining non-hydrogen atoms being located *via* standard Fourier technique; neutral atomic scattering factors; anomalous dispersion applied to all non-hydrogen atoms.

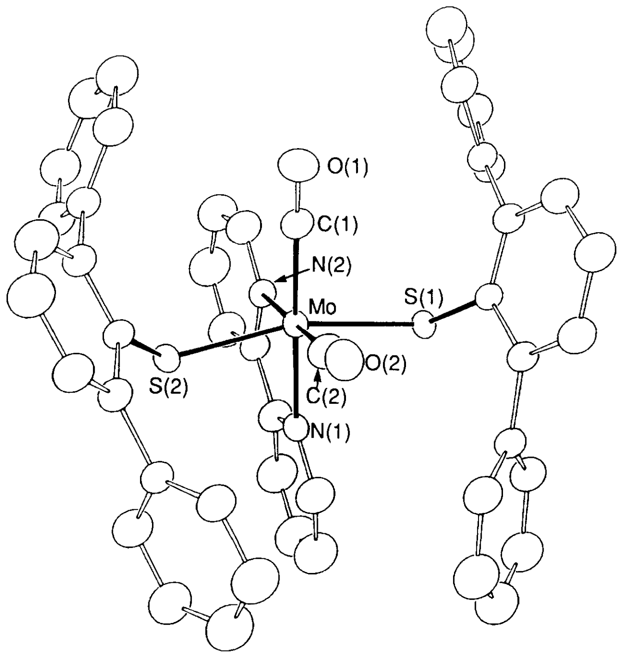
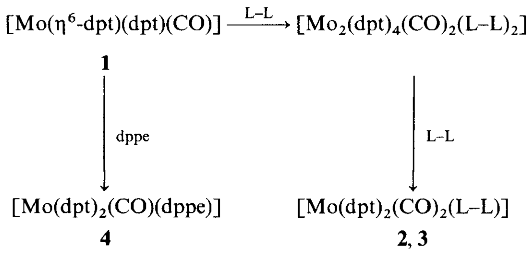


Fig. 5 An ORTEP view of complex **2**. Bond lengths (Å): Mo–S(1) 2.358(3), Mo–S(2) 2.343(3), Mo–N(1) 2.256(8), Mo–N(2) 2.244(7), Mo–C(1) 1.962(10), Mo–C(2) 1.964(10), C(1)–O(1) 1.150(13) and C(2)–O(2) 1.157(11). Bond angles (°): S(1)–Mo–S(2) 163.6(1), C(1)–Mo(1)–C(2) 75.2(4), N(1)–Mo–N(2) 72.0(3), Mo–C(1)–O(1) 175.5(8), Mo–C(2)–O(2) 172.5(9), Mo–S(1)–C(10) 111.7(3) and Mo–S(2)–C(20) 115.8(3)

arene ligand and a vacant site appropriate for a two-electron donor such as dinitrogen would be created. However, 1,2-dimethoxyethane solutions of complex **1** treated with excess of 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen) and 1,2-bis(diphenylphosphino)ethane (dppe) gave a series of novel molybdenum(II) thiolato-complexes, according to Scheme 1. A bridging CO complex is postulated as an intermediate in the formation of complexes **2** and **3** and is discussed below.



Scheme 1 L–L = bipy, **2**; or phen, **3**

Complexes **2** and **3** (red-purple) and **4** (pink) were synthesised in moderate yields (30–40%). They were isolated as powders by removal of the reaction solvent *in vacuo* and trituration of the resulting oils with diethyl ether. The remaining diethyl ether residue remained coloured but slowly bleached, suggesting that additional Mo-containing complexes were present, but these could not be isolated in a pure state. Complexes **2**–**4** were found to be neutral, diamagnetic and air-stable solids and were purified by chromatography on neutral alumina.

The IR spectra of the carbonyl species all show strong bands in the region 1800–2000 cm^{-1} assigned to ν(CO). One ν(CO) band was observed for complex **4** and two for **2** (1865 and 1955 cm^{-1}) and **3** (1840 and 1935 cm^{-1}). These last values are somewhat higher than for the structurally analogous *tert*-butyl alkoxide complex [Mo(OBu^t)$_2$(CO)$_2$(py)$_2$] [py = pyridine, ν(CO) 1898 cm^{-1}]. Chisholm *et al.*[17] proposed that the low values were due to enhanced π donation from the alkoxide ligands to the molybdenum(II) centre ($p_\pi \longrightarrow d_\pi$ donation)

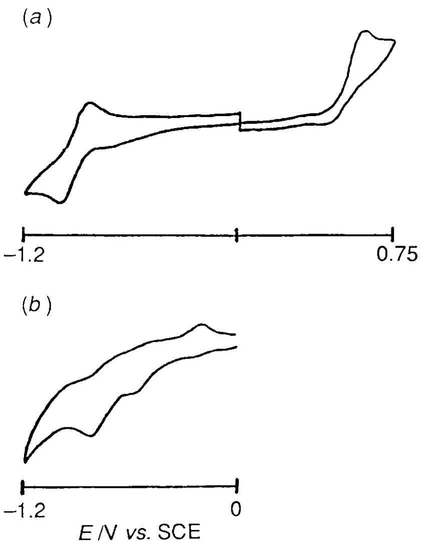


Fig. 6 (*a*) Cyclic voltammogram of complex **1**, at scan rate 0.5 V s^{-1}, platinum electrode, 0.2 mol dm^{-3} $[NBu_4][BF_4]$ in 1,2-dimethoxyethane, *ca.* 10^{-3} mol dm^{-3}. (*b*) As (*a*) but under an atmosphere of CO

which results in an increase in back bonding from the metal d orbitals to antibonding CO orbitals.[13] The higher values seen in the dicarbonylthiolato-complexes may reflect the known lower π-donating ability of thiolato-sulphur.

Proton, and where relevant, $^{31}P-\{^1H\}$, NMR data lend support to the formulations for complexes **2**–**4**. The $^{31}P-\{^1H\}$ NMR spectrum of **4** consists of one sharp singlet at 41 ppm. The magnitude of the chemical shift indicates that the phosphorus ligand is complexed to the metal and the appearance of a singlet implies that the two phosphorus atoms are in magnetically equivalent environments. Based on these data, a probable structure for complex **4** would be a trigonal-bipyramidal arrangement of ligands with axial thiolate ligands.

X-Ray Structure of $[Mo(dpt)_2(CO)_2(bipy)]$ **2**.—The molecular structure of $[Mo(dpt)_2(CO)_2(bipy)]$ **2** is shown in Fig. 5 together with relevant bond lengths and angles. Table 4 lists the atomic coordinates.

The geometry about the Mo^{II} is distorted octahedral comprising two *trans*-axial thiolato-ligands, equatorially located *cis*-carbonyl ligands, and a *cis*-bipyridyl ligand. The distortion from an ideal octahedron is a consequence of a small 'bite' angle for the bipy ligand that results in an acute N(1)–Mo–N(2) angle of 72°. The orientation of the *trans*-carbonyl ligands also results in an acute 'inter-ligand' angle [C(1)–Mo–C(2) 75°]. Analogous bond angles were also observed for the structurally similar molybdenum(II) complex $[Mo(OBu^t)_2(CO)_2(py)_2]$[17] where N(1)–Mo–N(2) 85° and C(1)–Mo–C(2) 72°. In contrast, $[MoBr_2(CO)_2(PPh_3)_2]$,[18] containing equatorial *cis*-bromide and *trans*-carbonyl ligands, has Br–Mo–Br 83.1(2) and C(1)–Mo–C(2) 119.4(24)°. In all three of these structures the axial ligands are distorted from the ideal 180°, with $[MoBr_2(CO)_2(PPh_3)_2]$ the most dramatic, P(1)–Mo–P(2) 127.8(4)°. In contrast, $[Mo(OBu^t)_2(CO)_2(py)_2]$ has O(3)–Mo–O(4) 156° and for complex **2**, S(1)–Mo–S(2) 163.6(1)°. Comparison of Mo–C bond distances for the three complexes shows that $[MoBr_2(CO)_2(PPh_3)_2]$ has the shortest at 1.85 Å (average) and, not surprisingly, $[Mo(OBu^t)_2(CO)_2(py)_2]$ (1.94 and 1.95 Å) and complex **2** [1.962(10) and 1.964(10) Å] have similar lengths. The C–O bonds are similar in all three complexes with values ranging from 1.15 to 1.17 Å.

Formation of the dicarbonyl complex $[Mo(dpt)_2(CO)_2(bipy)]$ from the monocarbonyl species $[Mo(\eta^6\text{-dpt})(dpt)(CO)]$ **1** was monitored using solution IR spectroscopy of reaction mixtures. By addition of 1 mol equivalent of bipy to complex **1** in CH_2Cl_2, three different carbonyl-containing species were found. In the IR spectrum of the carbonyl region for the solution from the above reaction a band at 1930 cm^{-1} is due to unreacted starting material (complex **1**), those at 1955 and 1865 cm^{-1} can be assigned to the dicarbonyl final product $[Mo(dpt)_2(CO)_2(bipy)]$ **2** and a bond at 1835 cm^{-1} is of low enough frequency to suggest the presence of bridging-carbonyl ligands. A band at approximately 1600 cm^{-1} is associated with the 2,6-diphenylthiophenolate ligands. Further addition of bipy (2 mol equivalents) resulted in the complete formation of $[Mo(dpt)_2(CO)_2(bipy)]$ and the disappearance of all the bands assigned to the bridging intermediate carbonyl species and starting material. The structure of the proposed intermediate species is unknown. However, it is feasible that excess of bipy or phen initiates asymmetric cleavage of the μ-CO bonds to form complexes **2** and **3**. The overall yield of the latter complexes is less than 50% and is in accord with the above proposal. The fate of the non-carbonyl-containing molybdenum complex also formed by addition of excess of ligand is unknown. However, a dark solution remains after isolation of $[Mo(dpt)_2(CO)_2(bipy)]$ and contains no ν(CO) bands in its IR spectrum, consistent with the proposed mechanism.

Electrochemistry of Complex **1**.—The redox behaviour of the green η^6-arene complex **1** was studied at a platinum-disc electrode in 0.2 mol dm^{-3} $[NBu_4][BF_4]$–CH_2Cl_2 under an atmosphere of argon. The resulting cyclic voltammogram is shown in Fig. 6, and displays a reversible reduction at $E_{\frac{1}{2}} = -1.04$ V and an irreversible oxidation at $E_p^{ox} = +0.55$ V (both *vs.* saturated calomel electrode, SCE). The reversibility of the reduction couple is indicated by the near-unity value for the ratio i_{p_a}/i_{p_c} over the scan range 0.1–5 V s^{-1} and the independence of the current function $(i_p/c^{\frac{1}{2}})$ with the scan rate. The peak separations (ΔE_p) are in the range 100–130 mV (scan range 0.1–5 V s^{-1}) and are relatively large. However, under the same experimental conditions, ΔE_p for the ferrocene–ferrocenium couple (a known one-electron reversible oxidation process) at a scan rate of 0.5 V s^{-1} was 108 mV and suggests uncompensated internal resistance may be responsible for the large ΔE_p values. The magnitude of the ΔE_p values suggests a one-electron reduction process to form a molybdenum(I) anionic species. Running the experiment under an atmosphere of dinitrogen gave the same cyclic voltammogram as that seen in Fig. 6. This was also the case under 10 atm dinitrogen, indicating no reactivity of the anion towards this substrate. Metal reduction is most likely to strengthen bonding of the η^6-arene ligand to the metal centre and hence decrease its lability.

The irreversibility of the oxidation process at $E_p^{ox} = +0.55$ V is probably due to decomposition of the oxidised η^6-arene complex *via* loss of CO. This is consistent with results obtained from the oxidation of complex **1** with Br_2 to form a non-carbonyl-containing product (determined by IR spectroscopy). If the cyclic voltammogram is run under an atmosphere of CO complicated redox behaviour occurs, mainly seen as irreversible reduction processes [Fig. 6(*b*)], presumably due to generation of the purple polycarbonyl species described earlier.

Experimental

Synthesis of complexes and ligands were routinely carried out under N_2 using standard Schlenk-line techniques and solvents freshly distilled over suitable drying agents prior to use. The complex $[MoCl_2(CO)_4]$[19] was synthesised according to the literature method, and 2,6-diphenylthiophenol was prepared by the Newman–Kwart rearrangement[20] from the corresponding phenol (Aldrich). The compound $RhCl_3 \cdot 3H_2O$ was used as obtained from Johnson Matthey.

Proton and $^{31}P-\{^1H\}$ NMR spectra were recorded on a Bruker WP80 SY instrument at 80 and 32.4 MHz respectively in $CDCl_3$ solutions using $SiMe_4$ (^1H) and H_3PO_4 (^{31}P) as internal references (0.0 ppm). Infra-red spectra were obtained from Nujol mulls between KBr discs using a Perkin-Elmer 1330 IR spectrophotometer, UV–VIS spectra on a SP-1800 UV spectrophotometer for CH_2Cl_2 solutions using quartz cells having a pathlength of 1 cm. Elemental analyses were obtained from the Micro-analytical Laboratory, the University of Manchester.

Cyclic voltammetric measurements were made on an EG and G PAR model 362 scanning potentiostat. A three-electrode cell configuration was used with a platinum-disc working electrode and tungsten-wire secondary electrode, arranged such that a luggin capillary was in close proximity to the working electrode. Potentials were quoted *versus* the saturated calomel electrode (SCE), against which the ferrocene–ferrocenium couple has a $E_{\frac{1}{2}}$ value of +0.54 V in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$.

Details of X-ray crystallographic data can be found in Table 5. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

2,6-*Diphenylthiophenol.—Step* 1, O-(2,6-*diphenyl*)*phenyl* N,N-*dimethylthiocarbamate*. Sodium hydride (7.8 g, 0.32 mol) was added to a solution of 2,6-diphenylphenol (74 g, 0.3 mol) in dimethyl formamide (200 cm^3). The reaction mixture was stirred vigorously during the addition to allow for the rapid evolution of H_2. When gas evolution had ceased dimethylthiocarbamoyl chloride (30 g, 0.3 mol) was added, the reaction mixture heated (*ca.* 100 °C, 2 h) and then cooled to room temperature. The resulting mixture was poured into a 2% solution of aqueous KOH (1 l), and the resulting precipitate was filtered under suction. The crude product was recrystallised from hot ethanol to give 30 g (30% yield) of *O*-(2,6-diphenyl)phenyl *N,N*-dimethylthiocarbamate, m.p. 130–133 °C (Found: C, 76.1; H, 5.6; N, 4.0. $C_{21}H_{19}NOS$ requires C, 76.1; H, 5.7; N, 4.2%); ν_{max}(C=S)/cm^{-1} 1200s (Nujol)

Step 2, S-(2,6-*diphenyl*)*phenyl* N,N-*dimethylthiocarbamate*. *O*-(2,6-Diphenyl)phenyl *N,N*-dimethylthiocarbamate (30 g, 0.09 mol) was heated (*ca.* 250 °C) using a heating mantle and the flask fitted with a nitrogen bubbler and a slow mechanical stirrer. The reaction was monitored by occasionally taking drops of liquid from the reaction vessel for IR spectroscopic analysis. When the ν(C=S) band had disappeared the rearrangement reaction was complete (*ca.* 20 h). The liquid was then allowed to cool to room temperature and the resulting solid recrystallised from hot industrial methylated spirit (yield = 30 g, 100%); ν_{max}(C=O)/cm^{-1} 1675s (Nujol).

Step 3, *reduction and hydrolysis*. To a suspension of lithium aluminium hydride (15 g, 0.4 mol) in dry diethyl ether (200 cm^3) was added over a period of *ca.* 1 h the product (30 g) from the previous step. After addition was complete the reaction mixture was heated to reflux temperature for 3 h, then allowed to cool to room temperature. Excess of $LiAlH_4$ still present was destroyed by dropwise addition of water, and the mixture was then added slowly to an acidified ice slurry (1 l) whilst stirring vigorously. A solution of 2 mol dm^{-3} H_2SO_4 was then added and the solid which formed was filtered off under suction. Recrystallisation of the product from hot industrial methylated spirit and a small amount of water gave crystals of 2,6-diphenylthiophenol (yield = 10 g, 13% overall), m.p. 78 °C (Found: C, 82.1; H, 5.50%; M^+ 260. $C_{18}H_{14}S$ requires C, 82.4; H, 5.5%; *M* 260); ν_{max}(SH)/cm^{-1} 2580w (Nujol); δ_H (CD_2Cl_2) 3.4 (1 H, s, SH) and 7.2, 7.4 (13 H, m, aryl).

[Mo(η^6-dpt)(dpt)(CO)] **1**.—Sodium 2,6-diphenylthiophenolate (2.0 g, 7.1 mmol) dissolved in 1,2-dimethoxyethane (20 cm^3) was added dropwise to a solution of $[MoCl_2(CO)_4]$ (1 g, 3.6 mmol) in 1,2-dimethoxyethane (30 cm^3) and stirred for 12 h. The green-yellow solution was filtered through Celite and the filtrate evaporated to dryness. The resulting green-yellow oil was triturated with warm hexane for 5 min to yield the complex as a green powder (yield = 1.6 g, 73.3%).

$[Mo(dpt)_2(CO)_2(bipy)]$ **2**.—Excess of 2,2′-bipyridyl (0.1 g, 0.85 mmol) was added to a solution of the η^6-arene complex **1** (0.18 g, 0.3 mmol) in 1,2-dimethoxyethane giving an immediate dark purple solution. After *ca.* 3 h the solution was evaporated to dryness and the residue chromatographed on a neutral alumina column (1 × 30 cm length) using dichloromethane as the solvent. The dark purple band was eluted and collected and the dichloromethane removed under reduced pressure to yield an oil that was triturated with diethyl ether. A purple powder resulted that was filtered off and dried *in vacuo* (0.1 Torr) (yield = 0.02 g, 20%).

$[Mo(dpt)_2(CO)_2(phen)]$ **3**.—Complex **3** was prepared in an analogous manner to **2** except that 1,10-phenanthroline (0.1 g, 0.56 mmol) was used (yield = 0.11 g, 70%).

$[Mo(dpt)_2(CO)(dppe)]$ **4**.—Excess of 1,2-bis(diphenylphosphino)ethane (1.2 g, 3.0 mmol) was added to a green solution of the η^6-arene complex **1** (0.1 g, 1.15 mmol) in 1,2-dimethoxyethane (30 cm^3) to give an immediate dark pink solution. After stirring for *ca.* 12h the solvent was removed under reduced pressure (0.1 Torr, *ca.* 60 °C) and the resulting pink oil triturated with diethyl ether. The end product, a pink powder, was filtered off and dried *in vacuo* (0.1 Torr) (yield = 0.067 g, 60%).

$[Rh_2\{\mu\text{-}SC_6H_3(C_6H_4)\text{-}2\text{-}Ph\text{-}6\}_2(dpt)_2(NCMe)_2]$ **5**.—To a suspension of $RhCl_3{\cdot}3H_2O$ (0.16 g, 0.61 mmol) in acetonitrile (30 cm^3) was added 6 mol equivalents of 2,6-diphenylthiophenol (0.94 g, 3.6 mmol) and an equivalent amount of triethylamine (0.36 g, 3.6 mmol). The suspension changed immediately to a dark red solution. After stirring for *ca.* 12 h a red powder had precipitated from the acetonitrile reaction mixture, which was collected by filtration and dried *in vacuo* (0.1 Torr) (yield = 0.23 g, 30%).

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