

A novel Redox/Fission reaction of the molybdenum tetracarbonyl complex of 3-diphenylphosphino-(1*R*)-(+) -camphor dimethylhydrazone.

Crystal structure of $[\text{Mo}(\text{CO})_4(\text{PPh}_2\text{C}_{10}\text{H}_{15}\text{NH})]^*$

Sarath D. Perera, Bernard L. Shaw and Mark Thornton-Pett

School of Chemistry, The University of Leeds, Leeds LS2 9JT (UK)

(Received August 5, 1991)

Abstract

Treatment of the molybdenum tetracarbonyl complex of 3-diphenylphosphino-(1*R*)-(+) -camphor dimethylhydrazone $[\text{Mo}(\text{CO})_4(\text{PPh}_2\text{C}_{10}\text{H}_{15}\text{NNMe}_2)]$ (**1a**) with hydrogen chloride effects a rapid Redox/Fission reaction to give the molybdenum(II) imine complex $[\text{Mo}(\text{CO})_3\text{Cl}_2(\text{PPh}_2\text{C}_{10}\text{H}_{15}\text{NH})]$ (**2a**). Other strong acids HX reacted similarly to give analogous complexes $[\text{Mo}(\text{CO})_3\text{X}_2(\text{PPh}_2\text{C}_{10}\text{H}_{15}\text{NH})]$ (X = Br, I or OOCF₃). Reduction of **2a** with sodium borohydride in the presence of carbon monoxide gave $[\text{Mo}(\text{CO})_4(\text{PPh}_2\text{C}_{10}\text{H}_{15}\text{NH})]$ (**1b**), the crystal structure of which was determined. Treatment of **1b** with LiN(SiMe₃)₂, followed by MeI gave $[\text{Mo}(\text{CO})_4(\text{PPh}_2\text{C}_{10}\text{H}_{15}\text{NMe})]$ (**1c**). Treatment of **1a** with bromine gave the tricarbonylmolybdenum(II) complex $[\text{Mo}(\text{CO})_3\text{Br}_2(\text{PPh}_2\text{C}_{10}\text{H}_{15}\text{NNMe}_2)]$ (**2e**). NMR and IR data, and bond length/bond angle data for **1b**, are given.

Introduction

In a previous paper [1], we have described the synthesis of (1*R*)-(+) -camphor dimethylhydrazone and its conversion into the 3-*exo*-diphenylphosphino derivative. When this phosphine was treated with $[\text{Mo}(\text{CO})_4(\text{norbornadiene})]$ the norbornadiene was displaced and a complex $[\text{Mo}(\text{CO})_4(\text{PPh}_2\text{C}_{10}\text{H}_{15}\text{NNMe}_2)]$ was formed, with a 6-membered chelate ring and with the stereochemistry around the C=N bond *Z*. However, when this complex was heated in solution at 160°C, it isomerised to give $[\text{Mo}(\text{CO})_4(\text{PPh}_2\text{C}_{10}\text{H}_{15}\text{NNMe}_2)]$ (**1a**), containing a 5-membered chelate ring; in this complex the stereochemistry around the C=N bond was shown to be *E* by a crystal structure determination.

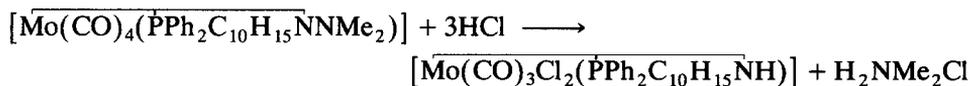
Correspondence to: Professor B.L. Shaw, School of Chemistry, The University of Leeds, Leeds LS2 9JT, UK.

* This paper is dedicated to the outstanding chemist Professor Akio Yamamoto upon his retirement from the Tokyo Institute of Technology.

In the present paper we describe some novel chemistry of the molybdenum(0) complex **1a**. This complex has a free NMe₂ group and we anticipated that, when treated with acids the nitrogen of this NMe₂ group should protonate, although it was conceivable that the molybdenum centre might protonate instead. We therefore treated a dichloromethane solution of the molybdenum(0) complex **1a** with hydrogen chloride and followed the progress of the reaction by ³¹P-{¹H} NMR spectroscopy.

Results and discussion

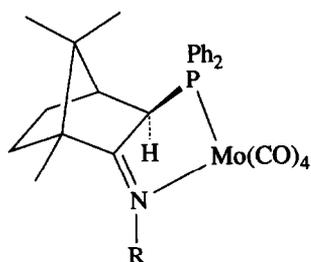
On passage of hydrogen chloride the complex **1a**, characterised by a ³¹P NMR chemical shift of δ 57.5 ppm, was very rapidly (< 1 min) converted into a single product, characterised by a singlet ³¹P resonance at δ 84.9 ppm. On a preparative scale an orange product was isolated in high yield and elemental analysis indicated a composition of C₂₅H₂₆Cl₂MoNO₃P (see Experimental) *i.e.* one nitrogen had been lost. From the ¹H NMR spectrum the three camphor methyl groups were still present (Table 1) but the NMe₂ group was absent. The C³-H proton gave a doublet of doublets at 5.2 ppm with ²J(PH) 14.3 and ⁴J(HH) 2.4 Hz. Of particular interest was a broad singlet at 8.98 ppm, corresponding to one hydrogen, which we assign to N-H. The infrared spectrum showed three very intense carbonyl absorptions, $\nu(\text{C}\equiv\text{O})$ at 2065, 1985 and 1910 cm⁻¹, *i.e.* at higher frequencies than those given by the molybdenum(0) complex **1a** but in the expected range for a tricarbonyl derivative of molybdenum(II) [2-4]. In particular, in the infrared spectrum, there was a medium to strong, sharp band at 3295 cm⁻¹, which we assign to $\nu(\text{N-H})$ and a band at 1645 cm⁻¹ due to $\nu(\text{C=N})$. Thus we assign structure [Mo(CO)₃Cl₂(PPh₂C₁₀H₁₅NH)] (**2a**) to this compound. We were unable to grow crystals of this complex suitable for a single-crystal X-ray diffraction study. However, as described below, we were able to convert it into [Mo(CO)₄(PPh₂C₁₀H₁₅NH)] (**1b**), the crystal structure of which was determined (see below). We formulate the reaction of the molybdenum(0)-phosphine-dimethylhydrazone complex **1a** with HCl to give the molybdenum(II)-phosphine-imine complex **2a** as



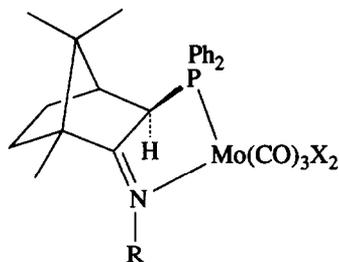
This Redox/Fission reaction is unusual and occurs rapidly under very mild conditions.

We found that other strong acids reacted similarly. Thus treatment of [Mo(CO)₄(PPh₂C₁₀H₁₅NNMe₂)] (**1a**) with HBr, HI or CF₃COOH gave [Mo(CO)₃X₂(PPh₂C₁₀H₁₅NH)] with X = Br (**2b**), I (**2c**) or OOCF₃ (**2d**), respectively. The ditrifluoroacetate **2d** was particularly easy to isolate (87% yield). Details of the conversions and elemental analytical data are given in the Experimental and ¹H NMR (Table 1); ³¹P-{¹H} NMR and IR data (Table 2) are also given.

It was possible to do a metathetical replacement reaction on the molybdenum(II) complexes of type **2**. We treated the ditrifluoroacetate **2d** with lithium bromide in acetone and isolated the corresponding dibromide **2b** in 74% yield (see Experimental). We also converted [Mo(CO)₄(PPh₂C₁₀H₁₅NNMe₂)] (**1a**) into the imine-molybdenum(II) complex **2a** by treating its acetone solution with concentrated hydrochloric acid; the isolated yield of **2a** was 26%.



- 1a** R = NMe₂
1b R = H
1c R = Me



- 2a** R = H, X = Cl
2b R = H, X = Br
2c R = H, X = I
2d R = H, X = O₂CCF₃
2e R = NMe₂, X = Br

Free imines (C=NH) are rare but some chromium carbonyl complexes with ligands-containing imine groups are known *e.g.* [(OC)₅CrNH=CMe₂] [5], [(OC)₅CrNH=C(CH₂)_n] [6].

In view of the novel Redox/Fission reaction involved in the conversion of the molybdenum(0) complex **1a** to the molybdenum(II) complex **2a**, we also studied the addition of one mole of bromine or chlorine to the molybdenum(0) complex **1a**. Treatment with bromine gave a clean reaction and [Mo(CO)₃Br₂(PPh₂C₁₀H₁₅NNMe₂)] (**2e**) was isolated in 76% yield. Preparative details and elemental analytical data are given in the Experimental and characterising NMR and infrared data are given in Tables 1 and 2. The reaction of chlorine with **1a** was much less clean than the reaction of bromine and gave a mixture of two products, which we could not separate.

We have also studied the reduction of one of these novel tricarbonylmolybdenum(II)-phosphine-imine complexes of type **2**. Treatment of a suspension of **2a** in a tetrahydrofuran-ethanol mixture with sodium borohydride, in an atmosphere of carbon monoxide gave the tetracarbonylmolybdenum(0)-phosphine-imine complex **1b** in 88% yield. Preparative details, elemental analytical data and ¹³C NMR data are in the Experimental and NMR and infrared data in Tables 1 and 2. In particular, in the ¹H NMR spectrum (Table 1) a broad singlet at 8.74 ppm was assigned to NH and in the infrared spectrum a band at 3280 cm⁻¹ (Table 2) was assigned to ν(N-H). In the infrared spectrum the three carbonyl stretching frequencies, 2015, 1900 and 1845 cm⁻¹ are typical for a tetracarbonylmolybdenum(0) complex, *e.g.* [Mo(CO)₄(PPh₂C₁₀H₁₅NNMe₂)] (**1a**) shows ν(C=O) bands at 2025, 1910 and 1850 cm⁻¹ [1]. The mass spectrum of this complex showed a parent molecular ion over the range for *m/e* of 539 to 548 Daltons with the most intense peak at 545 Daltons, as expected for a complex of composition C₂₆H₂₆MoNO₄P, the breakdown pattern of the complex showed successive groups of peaks at M - 28, M - 56, M - 84 and M - 112 Daltons corresponding to loss of one, two, three and four carbonyl groups. In view of the fact that the Redox/Fission reaction is novel and that imine (C=NH)-metal complexes are relatively rare we have determined the crystal structure of [Mo(CO)₄(PPh₂C₁₀H₁₅NH)] (**1b**).

Table 1

¹H NMR data ^a (in complexes **1b**, **2a**, **2b**, **2c**, and **2d**, *J*(HH) refers to four-bond coupling between C(3)-H and N-H, confirmed by double resonance experiments)

Complex	Camphor methyls	Others
1a	-0.21(s), 0.70(s), 1.28(s)	2.32(s, 3H, NMe ₂), 2.50(s, 3H, NMe ₂), 3.20(d, 1H, <i>J</i> (PH) 11.3, C(3)-H)
1b	-0.23(s), 0.76(s), 0.95(s)	3.08(dd, 1H, <i>J</i> (PH) 10.5, <i>J</i> (HH) 3.0, C(3)-H), 8.74(s, br, 1H, NH)
1c ^b	-0.18(s), 0.68(s), 1.24(s)	3.21(dq, 1H, <i>J</i> (PH) 11.3, <i>J</i> (HH) 2.4, C(3)-H), 3.70(dd, 3H, <i>J</i> (PH) 2.4, <i>J</i> (HH) 2.2, NMe)
2a	-0.31(s), 0.78(s), 1.01(s)	5.20(dd, 1H, <i>J</i> (PH) 14.3, <i>J</i> (HH) 2.4, C(3)-H), 8.98(s, br, 1H, NH)
2b	-0.30(s), 0.78(s), 1.02(s)	5.35(dd, 1H, <i>J</i> (PH) 14.5, <i>J</i> (HH) 2.4, C(3)-H), 8.93(s, br, 1H, NH)
2c	-0.29(s), 0.78(s), 1.01(s)	5.39(dd, 1H, <i>J</i> (PH) 14.2, <i>J</i> (HH) 2.5, C(3)-H), 8.88(s, br, 1H, NH)
2d ^c	-0.27(s), 0.80(s), 1.06(s)	4.67(dd, 1H, <i>J</i> (PH) 14.5, <i>J</i> (HH) 2.4, C(3)-H), 9.88(s, br, 1H, NH)
2e	-0.33(s), 0.71(s), 1.21(s)	2.99(s, 3H, NMe ₂), 3.13(s, 3H, NMe ₂), 5.44(d, 1H, <i>J</i> (PH) 16.9, C(3)-H)

^a Recorded at 100 MHz, chemical shifts (δ) in ppm (± 0.01 ppm) relative to high frequency of SiMe₄, solvent CDCl₃ unless other stated, coupling constants *J* in Hz (± 0.1 Hz), br = broad, s = singlet, d = doublet, dd = doublet of doublets, dq = doublet of quartets. ^b Recorded at 400 MHz. ^c In CD₂Cl₂.

Crystal structure of [Mo(CO)₄(PPh₂C₁₀H₁₅NH)] (**1b**)

The crystal structure of complex **1b** is shown in Fig. 1 and selected bond lengths and angles are shown in Table 3 and atom coordinates in Table 4. The structure shows that the PPh₂ group is in the *exo*-position, as found in the crystal structure of **1a** [1] and that the molybdenum is coordinated to nitrogen, *i.e.* NH. The hydrogen was not located but the NMR and infrared evidence given above clearly shows that it is present. The arrangement around the C=N bond is *E*, as in the structure of **1a**. The bond lengths in **1b** are generally similar to those in **1a** except that the N(1)-Mo distance 228.0(4) pm is significantly less in the NH complex **1b** than in the NNMe₂ complex **1a** (233.1(7) pm).

Table 2

³¹P-{¹H} NMR ^a and IR ^b data

Complex	$\delta(^{31}\text{P})$	$\nu(\text{C}=\text{N})^c$	$\nu(\text{N}-\text{H})^c$	$\nu(\text{C}=\text{O})^d$
1a	57.5 ^e	1610	-	2020, 1905, 1850
1b	64.5 ^e	1635	3280m	2015, 1900, 1845
1c	57.0	1630	-	2020, 1905, 1850
2a	84.9	1645	3295m	2065, 1985, 1910
2b	83.5	1645	3290m	2050, 1975, 1910
2c	80.4	1640	3250m	2040, 1975, 1920
2d	91.6 ^f	1650	3310m	2070, 1985, 1910
2e	70.6	1585	-	2050, 1975, 1910

^a Recorded at 40.25 MHz, chemical shifts (δ) in ppm (± 0.1 ppm) relative to high frequency of 85% H₃PO₄, solvent CDCl₃ unless otherwise stated. ^b In cm⁻¹. ^c KBr disc. ^d In CH₂Cl₂, all carbonyl bands are strong. ^e In CH₂Cl₂. ^f In CD₂Cl₂.

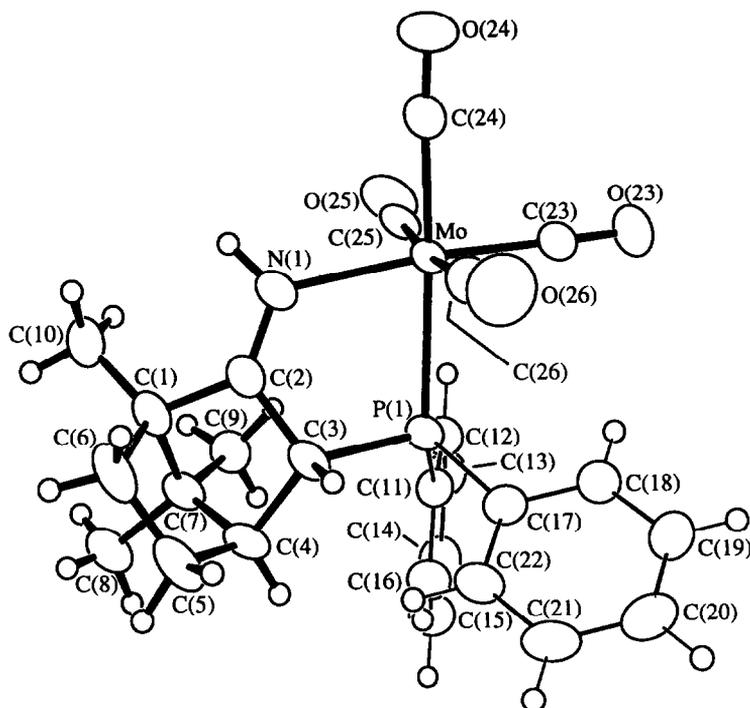


Fig. 1. ORTEP representation of the crystal and molecular structure of $[\overline{\text{Mo}(\text{CO})_4(\text{PPh}_2\text{C}_{10}\text{H}_{15}\text{NH})}]$ (**1b**).

We have also methylated the imine ($\text{C}=\text{NH}$) complex **1b** and converted it into the corresponding methylimine ($\text{C}=\text{NMe}$) complex **1c**. Treatment of the imine complex **1b** with lithium bis(trimethylsilyl)amide followed by addition of an excess of methyl iodide gave the hoped for methyl analogue **1c** in an isolated yield of 78%. This complex was characterised by elemental analysis and its $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum which showed as singlet resonance at δ 47.6 ppm assigned to NCH_3 and a doublet of doublet (3 hydrogens due to NCH_3) at 3.70 ppm with $^5J(\text{HH}) = 2.2$ and $^4J(\text{PH}) = 2.4$ Hz (Table 1) in its ^1H NMR spectrum. The infrared spectrum (Table 2), as expected, showed no band due to $\nu(\text{N}-\text{H})$. The mass spectrum showed the parent molecular ion over the range for m/e of 553 to 562 Daltons with the most intense peak at 559 Daltons, as expected for a complex of composition $\text{C}_{27}\text{H}_{28}\text{MoNO}_4\text{P}$.

Treatment of the imine complex **1b** with chlorine or bromine in dichloromethane solution gave back the molybdenum(II) complexes **2a** or **2b**, respectively, in good yields: see Experimental.

Experimental

The general techniques and apparatus were as described previously [7].

Preparation of $[\overline{\text{Mo}(\text{PPh}_2\text{C}_{10}\text{H}_{15}\text{NH})(\text{CO})_3\text{Cl}_2}]$ (**2a**)

Dry hydrogen chloride was bubbled through a solution containing complex **1a** (1.17 g, 2.0 mmol) in dichloromethane (15 cm^3) for 2 min. After 20 min the

Table 3

Selected bond lengths (pm) and angles (°) for compound **1b** with estimated standard deviations (e.s.d.'s) in parentheses

P(1)–Mo(1)	251.9(4)	N(1)–Mo(1)	228.0(4)
C(23)–Mo(1)	195.0(5)	C(24)–Mo(1)	199.3(5)
C(25)–Mo(1)	203.5(5)	C(26)–Mo(1)	202.4(5)
C(2)–C(1)	150.7(6)	C(6)–C(1)	155.9(6)
C(7)–C(1)	156.3(6)	C(10)–C(1)	151.6(7)
C(3)–C(2)	151.0(6)	N(1)–C(2)	128.1(5)
C(4)–C(3)	155.0(5)	C(5)–C(4)	154.7(6)
C(7)–C(4)	156.3(7)	C(6)–C(5)	155.0(8)
C(8)–C(7)	152.9(6)	C(9)–C(7)	154.2(6)
O(23)–C(23)	117.2(5)	O(24)–C(24)	114.7(5)
O(25)–C(25)	114.2(5)	O(26)–C(26)	115.4(5)
N(1)–Mo(1)–P(1)	77.0(2)	C(23)–Mo(1)–P(1)	96.7(2)
C(23)–Mo(1)–N(1)	171.3(1)	C(24)–Mo(1)–P(1)	172.1(1)
C(24)–Mo(1)–N(1)	99.1(2)	C(24)–Mo(1)–C(23)	87.8(2)
C(25)–Mo(1)–P(1)	98.7(2)	C(25)–Mo(1)–N(1)	86.6(2)
C(25)–Mo(1)–C(23)	88.5(2)	C(25)–Mo(1)–C(24)	87.8(2)
C(26)–Mo(1)–P(1)	87.0(2)	C(26)–Mo(1)–N(1)	98.0(2)
C(26)–Mo(1)–C(23)	87.4(2)	C(26)–Mo(1)–C(24)	86.8(2)
C(26)–Mo(1)–C(25)	173.4(1)	C(6)–C(1)–C(2)	106.4(3)
C(7)–C(1)–C(2)	98.2(3)	C(7)–C(1)–C(6)	101.6(4)
C(10)–C(1)–C(2)	115.8(3)	C(10)–C(1)–C(6)	114.8(4)
C(10)–C(1)–C(7)	117.7(4)	C(3)–C(2)–C(1)	107.9(3)
N(1)–C(2)–C(1)	130.9(3)	N(1)–C(2)–C(3)	121.0(3)
C(2)–C(3)–P(1)	111.0(3)	C(4)–C(3)–P(1)	127.0(3)
C(4)–C(3)–C(2)	101.6(4)	C(5)–C(4)–C(3)	104.7(3)
C(7)–C(4)–C(3)	102.8(3)	C(7)–C(4)–C(5)	101.5(4)
C(6)–C(5)–C(4)	103.3(3)	C(5)–C(6)–C(1)	104.4(4)
C(4)–C(7)–C(1)	94.4(3)	C(8)–C(7)–C(1)	114.6(4)
C(8)–C(7)–C(4)	113.4(3)	C(9)–C(7)–C(1)	112.0(3)
C(9)–C(7)–C(4)	115.2(3)	C(9)–C(7)–C(8)	107.2(3)
C(2)–N(1)–Mo(1)	123.2(3)	O(23)–C(23)–Mo(1)	178.0(3)
O(24)–C(24)–Mo(1)	176.2(3)	O(25)–C(25)–Mo(1)	175.1(2)
O(26)–C(26)–Mo(1)	174.4(3)		

solution was evaporated to a low volume under reduced pressure. Addition of methanol to the residue gave the required product **2a** as orange microcrystals; yield (0.95 g, 81%).

Found: C, 50.85; H, 4.45; N, 2.4; Cl, 12.8; $C_{25}H_{26}Cl_2MoNO_3P \cdot 0.1(CH_2Cl_2)$ calc.: C, 50.7; H, 4.45; N, 2.35; Cl, 13.1%.

Preparation of $[Mo(\overline{PPh_2C_{10}H_{15}NH})(CO)_3Br_2]$ (**2b**)

Hydrobromic acid (60% w/w HBr) (0.25 cm³) was added to a solution of complex **1a** (80 mg, 0.13 mmol) in acetone (2 cm³). After 30 min, the solvent was removed and the residue was crystallised from acetone-methanol to give the required product **2b** as yellow microcrystals; yield (42 mg, 47%).

Found: C, 44.35; H, 3.9; N, 2.25; $C_{25}H_{26}Br_2MoNO_3P$ calc.: C, 44.45; H, 3.9; N, 2.05%.

Table 4

Atom coordinates ($\times 10^4$) for compound **1b** with e.s.d.'s in parentheses

Atom	x	y	z
Mo(1)	2101.8(2)	1000 ^a	-2032.3(2)
P(1)	3448.2(8)	1921.3(5)	361.1(7)
C(1)	3567(3)	-525(2)	2461(3)
C(2)	2905(3)	101(2)	1101(3)
C(3)	3065(3)	1121(2)	1614(3)
C(4)	4066(3)	1011(3)	3318(3)
C(5)	2924(4)	653(3)	3871(4)
C(6)	2533(4)	-370(3)	3237(4)
C(7)	5021(3)	90(2)	3456(3)
C(8)	5947(4)	-265(3)	5055(3)
C(9)	6158(3)	161(2)	2800(3)
C(10)	3828(4)	-1556(2)	2206(4)
N(1)	2401(3)	-103(2)	-275(2)
C(11)	5504(1)	2268(2)	1312(2)
C(12)	6469(1)	1991(2)	713(2)
C(13)	8047(1)	2204(2)	1461(2)
C(14)	8660(1)	2693(2)	2809(2)
C(15)	7694(1)	2970(2)	3408(2)
C(16)	6116(1)	2757(2)	2659(2)
C(17)	2525(2)	3043(1)	419(2)
C(18)	2361(2)	3706(1)	-665(2)
C(19)	1689(2)	4589(1)	-709(2)
C(20)	1182(2)	4809(1)	330(2)
C(21)	1346(2)	4146(1)	1414(2)
C(22)	2018(2)	3263(1)	1458(2)
C(23)	2168(3)	1999(2)	-3331(3)
O(23)	2241(3)	2585(2)	-4116(3)
C(24)	802(3)	246(2)	-3852(3)
O(24)	51(3)	-145(2)	-4945(3)
C(25)	3997(3)	406(2)	-2044(3)
O(25)	5005(3)	76(2)	-2159(3)
C(26)	103(3)	1590(2)	-2280(3)
O(26)	-1055(3)	1952(2)	-2533(3)

^a Coordinate fixed to define origin.*Preparation of [Mo($\overline{PPh_2C_{10}H_{15}NH}$)(CO)₃I₂] (2c)*

The complex **2c** was prepared and isolated in an analogous manner to complex **2b** using hydroiodic acid (55% w/w HI) and 20 h of reaction time; yield 37%.

Found: C, 38.85; H, 3.35; N, 1.6; C₂₅H₂₆I₂MoNO₃P calc.: C, 39.05; H, 3.40; N, 1.8%.

Preparation of [Mo($\overline{PPh_2C_{10}H_{15}NH}$)(CO)₃(O₂CCF₃)₂] (2d)

An excess of trifluoroacetic acid (0.2 cm³) was added to a solution of complex **1a** (0.1 g, 0.17 mmol) in dichloromethane (2 cm³). Work up as for complex **2a** then gave the complex **2d** as yellow microcrystals; yield (0.11 g, 87%).

Found: C, 46.05; H, 3.55; N, 1.8; C₂₉H₂₆F₆MoNO₇P · 0.25(CH₂Cl₂) calc.: C, 46.05; H, 3.5; N, 1.8%.

*Preparation of $[\overline{Mo(PPh_2C_{10}H_{15}NNMe_2)}(CO)_3Br_2]$ (**2e**)*

A solution of bromine in carbon tetrachloride (0.4 cm³, containing 0.21 mmol of bromine) was added dropwise to a solution containing complex **1a** (0.118 g, 0.2 mmol) in dichloromethane (2 cm³) at 0°C. After 15 min the solution was evaporated to a low volume under reduced pressure. Addition of methanol to the residue then gave the required product **2e** as yellow microcrystals; yield (0.11 g, 76%).

Found: C, 44.5; H, 4.3; N, 3.7; C₂₇H₃₁Br₂MoN₂O₃P · 0.2(CH₂Cl₂) calc.: C, 44.4; H, 4.3; N, 3.8%.

*Preparation of $[\overline{Mo(PPh_2C_{10}H_{15}NH)}(CO)_4]$ (**1b**)*

An excess of sodium borohydride (0.2 g) was added to a suspension of complex **2a** (0.95 g, 1.62 mmol) in a carbon monoxide saturated solvent mixture of tetrahydrofuran (30 cm³). The reaction was carried out in an atmosphere of carbon monoxide. After 45 min the solution was evaporated to dryness and the residue was extracted into dichloromethane (3 × 15 cm³), which was then washed with water (20 cm³) and dried over anhydrous MgSO₄. Removal of the solvent and crystallisation of the residue from dichloromethane-methanol gave the required product **1b** as yellow microcrystals; yield (0.78 g, 88%).

Found: C, 57.15; H, 4.65; N, 2.4; C₂₆H₂₆MoNO₄P calc.: C, 57.45; H, 4.80; N, 2.6%. ¹³C-¹H NMR (CDCl₃): δ (ppm), 46.4 (d, C(4), ²J(PC) 5.7 Hz), 55.5 (d, C(3), ¹J(PC) 8.1 Hz), 201.9 (d, C(2), ²J(PC) 11.5 Hz), 207.5 (d, CO, ²J(PC) 5.9 Hz), 210.5 (d, CO, ²J(PC) 9.4 Hz), 217.4 (d, CO, ²J(PC) 34.5 Hz), 220.8 (d, CO, ²J(PC) 7.2 Hz).

Mass spectra: parent molecular ion 539 to 548 Daltons, most intense peak at 545 Daltons.

*Preparation of $[\overline{Mo(PPh_2C_{10}H_{15}NMe)}(CO)_4]$ (**1c**)*

A solution of lithium bis(trimethylsilyl)amide in tetrahydrofuran (0.33 cm³, 1 M) was added to a solution of complex **1b** (60 mg, 0.11 mmol) in dry tetrahydrofuran (1.5 cm³). After 15 min, an excess of iodomethane (0.5 cm³) was added. The solution was then evaporated to a low volume under reduced pressure. Addition of methanol to the residue then gave the required product as yellow microcrystals; yield (48 mg, 78%).

Found: C, 57.85; H, 5.0; N, 2.45; C₂₇H₂₈MoNO₄P calc.: C, 58.15; H, 5.05; N, 2.5%. ¹³C-¹H NMR (CDCl₃): δ (ppm), 45.9 (d, C(4), ²J(PC) 5.2 Hz), 47.6 (s, N-CH₃), 60.4 (d, C(3), ¹J(PC) 8.9 Hz), 189.4 (d, C(2), ²J(PC) 7.8 Hz), 207.6 (d, CO, ²J(PC) 6.0 Hz), 211.3 (d, CO, ²J(PC) 9.4 Hz), 216.5 (d, CO, ²J(PC) 34.5 Hz), 221.8 (d, CO, ²J(PC) 7.6 Hz).

Mass spectra: parent molecular ion 553 to 562, most intense peak 559 Daltons.

*Conversion of the ditrifluoroacetate complex **2d** into the dibromo complex **2b***

Complex **2d** (63 mg, 0.085 mmol) and lithium bromide (73 mg, 0.85 mmol) were stirred together in acetone (2 cm³) for 30 min. After the removal of solvent under reduced pressure, the residue was extracted into dichloromethane, from which complex **2b** was isolated in 74% yield.

Conversion of the imine-molybdenum(0) complex 1b into the molybdenum(II) complex 2a

A solution of chlorine (0.092 mmol) in carbon tetrachloride (0.16 cm³) was added to a solution of complex **1b** (50 mg, 0.092 mmol) in dichloromethane (1.5 cm³) at 0°C. Work up then gave complex **2a** in 56% yield.

Conversion of the molybdenum(0) complex 1b into the molybdenum(II) complex 2b

Similarly, addition of bromine solution to a solution of complex **1b** gave complex **2b** in 82% yield.

Single crystal X-ray diffraction analysis of 1b

All crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω/θ scan mode using an online profile fitting method [8] and graphite-monochromated Mo- K_{α} radiation. The data-set was corrected for absorption semi-empirically using azimuthal ψ scans.

The structure was determined via standard heavy atom (for the Mo atom) and Fourier difference techniques and was refined by full-matrix least-squares using the SHELX program system [9]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl groups were treated as rigid bodies with idealised hexagonal symmetry (C–C 139.5 pm). All hydrogen atoms were included in calculated positions (C–H 96 pm) and were refined with an overall isotropic thermal parameter. The weighting scheme $w = [\sigma^2(F_o) + 0.00045(F_o)^2]^{-1}$ was used. The absolute configuration of the structure was initially assumed from the known configuration of the D-camphor based phosphine ligand. It was later confirmed when refinement of the enantiomorphic complex led to significantly higher values of R and R_w . Final non-hydrogen atomic coordinates are given in Table 4.

Crystal data. C₂₆H₂₆MoNO₄P, $M = 543.41$, monoclinic, space group $P2_1$, a 975.8(1), b 1406.6(2), c 1017.2(1) pm, β 117.82(1)°, U 1.2348(3) nm³, $Z = 2$, D_x 1.46 Mg m⁻³, $\lambda(\text{Mo-}K_{\alpha})$ 71.069 pm, μ 6.116 cm⁻¹, $F(000) = 555.91$.

Data collection. $4.0 < 2\theta < 50.0^\circ$, 4103 data collected, 3223 with $I > 2.0 \sigma(I)$ considered observed, T 200 K.

Structure refinement. Number of parameters = 283, $R = 0.00164$, $R_w = 0.0241$.

Acknowledgements

We thank the S.E.R.C. for support, and Dr J.D. Vessey for high field ¹³C-¹H NMR spectra.

References

- 1 S.D. Perera, B.L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, (1991) 1183.
- 2 R. Colton and I.B. Tomkins, *Aust. J. Chem.*, 19 (1966) 1519.
- 3 J.R. Moss and B.L. Shaw, *J. Chem. Soc. (A)*, (1970) 595.
- 4 G.R. Dobson, I.W. Stolz and R.K. Sheline, *Adv. Inorg. Chem. Radiochem.*, 8 (1966) 1.
- 5 D. Sellmann and E. Thallmair, *Angew. Chem., Int. Ed. Engl.*, 14 (1975) 753.
- 6 E.O. Fischer and L. Knauss, *Chem. Ber.*, 103 (1970) 1262.
- 7 X.L.R. Fontaine, E.H. Fowles, T.P. Layzell, B.L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, (1991) 1519.
- 8 W. Clegg, *Acta Crystallogr., Sect. A*, 37 (1987) 22.
- 9 G.M. Sheldrick, SHELX76, Program System for X-Ray Structure Determination, University of Cambridge, Cambridge, England, 1976.