Reactivity of Cationic Molybdenum(II) Complexes. Part 4.[1a] Isolation and Crystal Structure Determination of *cis*-[Mo(CO)$_2$(η-C$_5$Me$_5$)(PPh$_3$)(N$_3$)] and *cis*-[Mo(CO)$_2$(η-C$_5$Me$_5$)(PPh$_3$)(NCO)] *

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The complex [Mo(CO)$_3$(η-C$_5$Me$_5$)(PPh$_3$)]BF$_4$ (**1**) reacts with NaN$_3$ in methanol solution to give a mixture of *cis*-[Mo(CO)$_2$(η-C$_5$Me$_5$)(PPh$_3$)(N$_3$)] (**2**) and *cis*-[Mo(CO)$_2$(η-C$_5$Me$_5$)(PPh$_3$)(NCO)] (**3**), which were separated as pure products by column chromatography. Pure (**3**) was also obtained by an independent route, *i.e.* by treating a methanol solution of (**1**) with cyanate ion. The solid-state structures of complexes (**2**) and (**3**) were determined by single-crystal *X*-ray diffraction: they are isomorphous, space group $P2_1/c$ (no. 14); for (**2**), a = 8.625(2), b = 18.655(9), c = 17.573(5) Å, β = 92.29(2)°, Z = 4, 3 315 independent data [$I_o > 2.5\sigma(I_o)$] refined to R = 0.032, R' = 0.034; for (**3**), a = 8.641(1), b = 18.547(3), c = 17.52(1) Å, β = 91.15(3)°, Z = 4, 2 045 independent data [$I_o > 2.5\sigma(I_o)$] refined to R = 0.044, R' = 0.046. Differences in the co-ordination geometry of the N$_3^-$ and NCO$^-$ ligands are discussed.

In recent papers[1,2] we reported the reaction of hydride donors with the 18-electron cationic complexes [M(CO)$_3$(η-C$_5$Me$_5$)(PR$_3$)]$^+$ (1; M = Cr or Mo). As a part of our programme to investigate the reactivity of co-ordinated CO and with a view to discriminating between the electrophilicity of CO ligands *cis* and *trans* to the phosphine ligand in systems like (1), we have studied the reactivity of (1) towards N$_3^-$ and are now able to report the complete characterization of *cis*-[Mo(CO)$_2$(η-C$_5$Me$_5$)(PPh$_3$)(NCO)] (3) and *cis*-[Mo(CO)$_2$(η-C$_5$Me$_5$)(PPh$_3$)(N$_3$)] (2). These products are formed *via* nucleophilic attack of N$_3^-$ on a co-ordinated CO and from a CO substitution reaction by N$_3^-$, respectively.

Results and Discussion

By treating [Mo(CO)$_3$(η-C$_5$Me$_5$)(PPh$_3$)]BF$_4$ (1)[1] with 1 equivalent of NaN$_3$ in methanol solution, the solution changes from yellow to red-orange in a few hours and red crystals start to precipitate within 1 d; i.r. spectra of the solution show complete disappearance of the absorption characteristic of (1) after 1 week. The red crystals obtained show i.r. bands at 2 240, 2 210, 2 040, 1 940, and 1 860 cm^{-1} (Nujol), suggesting the presence of a mixture of isocyanate and azide derivatives.[3] Column chromatography allowed separation of the two components of the mixture as pure products. The complex [Mo(CO)$_2$(η-C$_5$Me$_5$)(PPh$_3$)(N$_3$)] shows i.r. (Nujol) absorptions at 2 040s [ν_{asym}(NNN)], 1 940vs and 1 860s [ν(C–O)] cm^{-1}, while [Mo(CO)$_2$(η-C$_5$Me$_5$)(PPh$_3$)(NCO)] shows absorptions at 2 240m, 2 210s [ν_{asym}(NCO)], 1 950vs and 1 870s [ν(C–O)] cm^{-1}. The relative intensities of the C–O absorptions indicate that both complexes are the *cis* isomers.[4]

When complex (1) is treated with KNCO in methanol solution (3) forms quantitatively as a pure product within 2 d. The formation of (3) from the reaction of (1) with NaN$_3$ proceeds through N$_3^-$ attack at a carbonyl carbon atom,[5] while its formation from (1) and cyanate ion could occur either *via* NCO$^-$ attack at the carbonyl carbon or *via* substitution of a CO ligand.[6] Published data clearly showed that the second mechanism is operative in an analogous iron system.[6] The observation that the reaction of complex (1) with N$_3^-$ produces some (2), which can be formed only by CO substitution, is in accord with the mechanism reported in ref. 6 for this kind of reaction.

The i.r. spectrum of complex (3) (Nujol) shows two absorptions attributable to the molybdenum co-ordinated NCO group (2 240w and 2 210s cm^{-1}); a similar i.r. pattern was interpreted[7] as arising from a mixture of *cis* and *trans* isomers. We think it is more reasonable to explain these data by the presence of bond isomers containing O- and N-bonded NCO groups. The ^{1}H n.m.r. spectrum of (3) at 300 MHz shows a sharp singlet for C$_5$Me$_5$, while distinct signals were observed for [Re(CO)$_2$(η-C$_5$Me$_5$)X$_2$] *cis* and *trans* isomers.[8] Complexes (2) and (3) were always isolated as *cis* isomers, no trace of the *trans* isomers being detected; since *cis–trans* isomerization is often rapid in such systems,[8,9] (2) and (3) are probably the thermodynamic products of the reactions and their greater thermodynamic stability compared with *trans*-(2) and *trans*-(3) can be understood by considering that, in the absence of severe steric interactions, strong *trans*-effect ligands tend to be *cis*. The isomerization is rapid compared with the product formation rates; this prevented us from drawing conclusions about the electrophilicity of the CO molecules *cis* and *trans* to the Ph$_3$P ligand in complex (1).

Structural Characterization of Complexes (2) *and* (3).—The crystals of complexes (2) and (3) consist of discrete molecular units with no short intermolecular interactions. The two species are isomorphous. The structure of (2) is shown in Figure 1, and a comparative view of (2) and (3) in Figure 2. Relevant structural parameters are reported in Table 1.

Compounds (2) and (3) are d^4 molybdenum(II) complexes in which the C$_5$Me$_5$ group formally acts as a tridentate six-electron donor. The Mo atom is also bonded to two *cis*-CO groups, to a PPh$_3$, and to N$_3^-$ or NCO$^-$ in (2) and (3),

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* *cis*-Azido- and -cyanato-dicarbonyl(η-pentamethylcyclopentadienyl)-(triphenylphosphine)molybdenum(II)

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

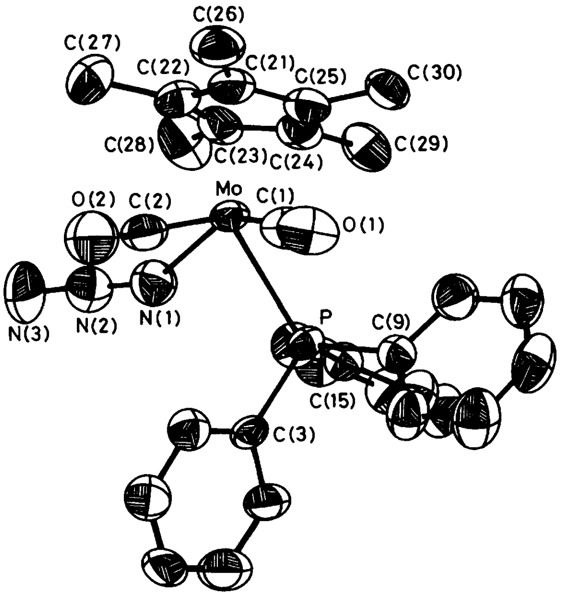

Figure 1. ORTEP drawing of complex (**2**) showing the atom numbering (H atoms are omitted for clarity)

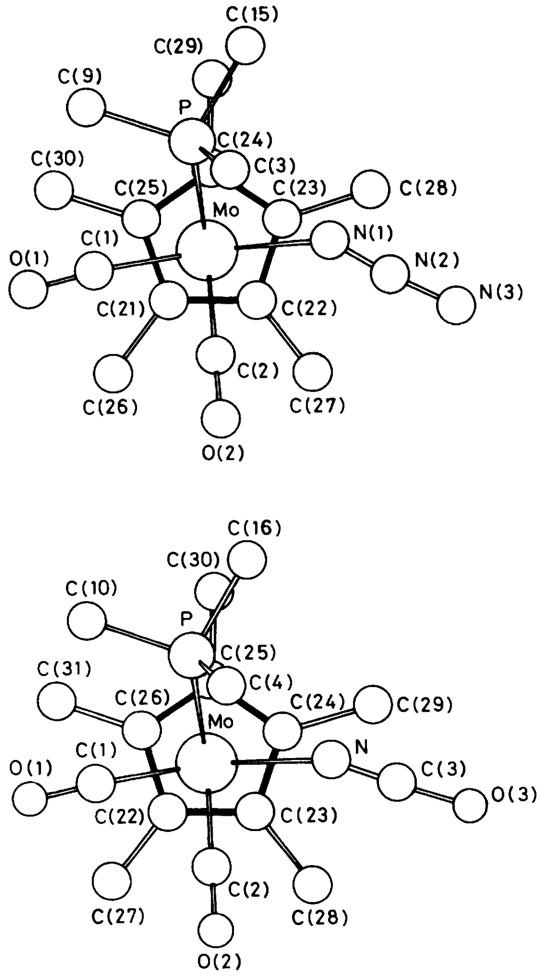

Figure 2. Comparison of the co-ordination geometry around the Mo atoms in complexes (2) and (3) (only P-bonded C atoms of the phenyl groups are shown)

Table 1. Selected bond distances (Å) and angles (°) for complexes (**2**) and (**3**)

(2)		(3)	
Mo–P	2.551(1)	Mo–P	2.549(2)
Mo–C(1)	1.976(4)	Mo–C(1)	1.95(1)
Mo–C(2)	1.937(4)	Mo–C(2)	1.93(1)
Mo–N(1)	2.142(4)	Mo–N	2.18(1)
Mo–C(21)	2.281(4)	Mo–C(22)	2.27(1)
Mo–C(22)	2.291(5)	Mo–C(23)	2.28(1)
Mo–C(23)	2.401(4)	Mo–C(24)	2.40(1)
Mo–C(24)	2.432(4)	Mo–C(25)	2.43(1)
Mo–C(25)	2.327(4)	Mo–C(26)	2.32(1)
C(1)–O(1)	1.14(1)	C(1)–O(1)	1.16(1)
C(2)–O(2)	1.16(1)	C(2)–O(2)	1.17(1)
N(1)–N(2)	1.14(1)	N–C(3)	1.12(1)
N(2)–N(3)	1.18(1)	C(3)–O(3)	1.24(1)
P–C(3)	1.836(4)	P–C(4)	1.83(1)
P–C(9)	1.826(4)	P–C(10)	1.83(1)
P–C(15)	1.838(4)	P–C(16)	1.84(1)
C(3)–C(4)	1.38(1)	C(4)–C(5)	1.37(1)
C(4)–C(5)	1.39(1)	C(5)–C(6)	1.39(1)
C(5)–C(6)	1.37(1)	C(6)–C(7)	1.36(2)
C(6)–C(7)	1.37(1)	C(7)–C(8)	1.39(2)
C(7)–C(8)	1.40(1)	C(8)–C(9)	1.36(1)
C(3)–C(8)	1.39(1)	C(4)–C(9)	1.40(1)
C(9)–C(10)	1.39(1)	C(10)–C(11)	1.39(1)
C(10)–C(11)	1.38(1)	C(11)–C(12)	1.38(2)
C(11)–C(12)	1.38(1)	C(12)–C(13)	1.37(2)
C(12)–C(13)	1.37(1)	C(13)–C(14)	1.37(2)
C(13)–C(14)	1.40(1)	C(14)–C(15)	1.40(1)
C(9)–C(14)	1.39(1)	C(10)–C(15)	1.40(1)
C(15)–C(16)	1.40(1)	C(16)–C(17)	1.39(1)
C(16)–C(17)	1.38(1)	C(17)–C(18)	1.39(1)
C(17)–C(18)	1.37(1)	C(18)–C(19)	1.39(2)
C(18)–C(19)	1.37(1)	C(19)–C(20)	1.34(1)
C(19)–C(20)	1.39(1)	C(20)–C(21)	1.38(1)
C(15)–C(20)	1.38(1)	C(16)–C(21)	1.37(1)
C(21)–C(26)	1.52(1)	C(22)–C(27)	1.50(1)
C(22)–C(27)	1.53(1)	C(23)–C(28)	1.56(2)
C(23)–C(28)	1.51(1)	C(24)–C(29)	1.52(1)
C(24)–C(29)	1.50(1)	C(25)–C(30)	1.50(1)
C(25)–C(30)	1.51(1)	C(26)–C(31)	1.52(1)
Mo–C(1)–O(1)	173.9(4)	Mo–C(1)–O(1)	175(1)
Mo–C(2)–O(2)	176.0(4)	Mo–C(2)–O(2)	176(1)
Mo–N(1)–N(2)	141.8(3)	Mo–N–C(3)	150(1)
N(1)–N(2)–N(3)	175.9(5)	N–C(3)–O(3)	177(1)
C(1)–Mo–N(1)	138.7(2)	C(1)–Mo–N	137.5(3)
C(2)–Mo–N(1)	81.3(2)	C(2)–Mo–N	79.5(3)
C(1)–Mo–C(2)	76.6(2)	C(1)–Mo–C(2)	75.5(4)
P–Mo–C(1)	79.1(1)	P–Mo–C(1)	79.3(3)
P–Mo–C(2)	110.5(1)	P–Mo–C(2)	110.2(3)
P–Mo–N(1)	76.6(1)	P–Mo–N	77.9(2)

respectively. The overall structure is most conveniently described as the well known 'four-legged piano-stool' geometry.[10] The Mo atoms in both (**2**) and (**3**) do not lie exactly over the centre of the C_5Me_5 ligands, as can be deduced from a comparison of the Mo–C(C_5Me_5) distances which range from 2.281(4) to 2.432(4) Å in (**2**) and from 2.27(1) to 2.43(1) Å in (**3**). This phenomenon seems to be a general feature of this type of complex: similar Mo–C distance distributions were found in (**1**) [2.29(1)—2.41(1) Å],[1b] $[Mo(CO)_2(\eta\text{-}C_5H_5)(PPh_3)(COMe)]$ [2.31(1)—2.38(1) Å],[11] $[Mo(CO)_2(\eta\text{-}C_5H_5)(PPh_3)\{C(CN)_2C(CN)_2Me\}]$ [2.300(3)—2.359(3) Å],[12] and $[Mo(CO)_2(\eta\text{-}C_5H_5)(PPh_3)I]$ [2.30(1)—2.37(1) Å].[13]

It is worth noting that in both complexes (**2**) and (**3**) the long Mo–C(C_5Me_5) distances are '*cis*' to the phosphine (see Figure 2) thus suggesting that steric factors may well be the reason for the observed deformations of the Mo–C_5Me_5 system. The fact that these deformations appear to be more appreciable in species containing C_5Me_5 ligands, such as (**1**)—(**3**), rather than C_5H_5 groups (see above), can easily be explained by the larger steric demand of the former ligands when the bulky PPh_3 group is present. These considerations are substantiated by the fact that the smaller '*trans*' angle at the molybdenum centre is not, as one would expect, the C–Mo–N one [138.7(2) in (**2**), 137.5(3)° in (**3**)], but rather the P–Mo–C angle [110.5(1) in (**2**), 110.2(3)° in (**3**)] although the latter involves the PPh_3 group. The ring carbon atoms are essentially coplanar [maximum deviation from the root-mean-square (r.m.s.) plane 0.016 Å in (**2**), and 0.14 Å in (**3**)]. However the methyl groups show an appreciable out-of-plane displacement [elevation from the r.m.s. plane of the C_5 ring ranging from 0.12 to 0.22 Å in (**2**), from 0.14 to 0.24 Å in (**3**)] bending 'away' from the Mo atoms. Carbon–carbon distances, within the C_5Me_5 ligands, show average values within the expected range [C–C(ring) 1.419(5), 1.41(1); C–C(Me) 1.51(1), 1.52(2) Å in (**2**) and (**3**), respectively]. The M–CO bonds show slight but significant deviation from linearity [Mo–C(1)–O(1) 173.9(4), 175(1); Mo–C(2)–O(2) 176.0(4), 176(1)° in (**2**), and (**3**), respectively].

The present structural study offers a unique opportunity of comparing the N_3^- and NCO^- ligand stereogeometries in two, almost identical, structural environments. Although the data for complex (**3**) are somewhat less accurate than those for (**2**) (see Experimental section), the differences in bond distances and angles between the two ligands appear to be significant. The Mo–N bond length in (**2**) [2.142(4) Å] is slightly shorter than in (**3**) [2.18(1) Å]. Moreover, while Mo–C and C–O distances for the *cis*-CO ligand are strictly equivalent in (**2**) and (**3**) [1.937(4), 1.93(1); 1.16(1), 1.17(1) Å, respectively] the lengthening of the Mo–N bond on passing from (**2**) to (**3**) is accompanied by an opposite effect on the M–C distances for the *trans*-CO ligands [1.976(4), 1.95(1), C–O 1.14(1), 1.16(1) Å]. This behaviour may be taken as indicative of a weaker σ-donor (stronger π-accepting) ability for N_3^- than for NCO^-, which results in a diminished π-back donation from the metal towards the *trans*-CO ligand.

The two bond sets within the two ligands are also noteworthy. As observed in other azido complexes,[14] the N–N–N system in (**2**) is not symmetric [N(1)–N(2) 1.14(1), N(2)–N(3) 1.18(1) Å], the short N–N bond being between the N atom in the middle and the N atom co-ordinated to the metal. This fact seems to contradict the observation[14] that complexes containing asymmetric azides have, in most cases, the metal-co-ordinated N atom involved in the long N–N bond. Unfortunately the paucity and poor reliability of the data on other complexes of this kind prevent a detailed analysis of these structural features. The Mo–N–N angle [141.8(3)°] falls within the wide range found in other species containing terminal azido groups [119[14]—167(1)°[15]], thus indicating that the M–N–N–N system possesses a remarkable structural flexibility.

Similar considerations might apply to the Mo–NCO system in (**3**), which shows larger differences in bond lengths [N–C(3) 1.12(1), C(3)–O(3) 1.24(1) Å] and a Mo–N–C(3) angle of 150(1)°. These values can be compared with those found in $[\overline{\mathrm{Pt(CH_2CH_2NHC}}{=}\mathrm{O)Cl(NCO)(tmen)}]$ (tmen = *N,N,N′,N′*-tetramethylethylenediamine) [1.11(2), 1.19(2) Å; 147(1)°],[16] $[Co(terpy)(NCO)_2]$ (terpy = 2,2′:6′,2″-terpyridyl) [1.13(1), 1.20(1) Å; 161(1)°],[17] and $[Mo_2(CO)_3(\eta\text{-}C_5Me_5)_2(\mu\text{-}NCMe_2)(NCO)]$ [Mo–N 2.06(1), N–C 1.16(2), C–O 1.18(2) Å; Mo–N–C 170(1)°].[18]

Both N–N–N and N–C–O groups approach linearity [175.9(5) and 177(1)°, respectively]. Finally, it should be mentioned that the occurrence of disorder in the crystal of complex (**3**) might be explained by assuming the presence of a small fraction (see Experimental section) of O-bonded NCO groups together with the N-bonded ones.

Experimental

All reactions were carried out by using standard Schlenk techniques under an atmosphere of purified nitrogen. Solvents were rendered water- and oxygen-free by distillation from an appropriate drying agent under nitrogen. The complex $[Mo(CO)_3(\eta\text{-}C_5Me_5)(PPh_3)]BF_4$ was prepared as reported.[1] Sodium azide and KNCO (both C. Erba) were used as purchased. I.r. spectra were recorded on a Perkin-Elmer 237-B spectrometer, ^1H n.m.r. spectra at 100 MHz on a Varian XL 100 spectrometer using $SiMe_4$ as internal standard.

Reaction of $[Mo(CO)_3(\eta\text{-}C_5Me_5)(PPh_3)]BF_4$ (**1**) *with* NaN_3.—A solution of NaN_3 (0.05 g, 0.77 mmol) in methanol (20 cm^3) was added while stirring at room temperature to the yellow solution obtained by dissolving complex (**1**) (0.5 g, 0.75 mmol) in methanol (30 cm^3). The colour of the solution turned to orange-red in a few hours and red crystals began to precipitate after 1 d. The reaction mixture was kept at room temperature for 1 week and then cooled to −70 °C and filtered. Red crystals were separated. Column chromatography (silica gel, toluene eluant) of the red crystals gave two fractions, the first containing $[Mo(CO)_2(\eta\text{-}C_5Me_5)(PPh_3)(N_3)]$ {66.5 mg, 15% yield, R_f = 0.2; i.r. (Nujol) ν_{asym}(NNN) 2 040s, ν(CO) 1 940vs, and 1860s cm^{-1}; ^1H n.m.r. [$(CD_3)_2CO$] 7.55—7.30 (m, 15 H, C_6H_5P) and 1.79 (s, 15 H, C_5Me_5)} (Found: C, 61.25; H, 5.10; N, 6.85. Calc. for $C_{30}H_{30}MoN_3O_2P$: C, 60.90; H, 5.10; N, 7.10%) and the second containing $[Mo(CO)_2(\eta\text{-}C_5Me_5)(PPh_3)(NCO)]$ {0.288 g, 65% yield, R_f = 0.1; i.r. (Nujol) ν_{asym}(NCO) 2 240w and 2 210s; ν(CO) 1 950vs and 1 870s cm^{-1}; ^1H n.m.r. [$(CD_3)_2CO$] 7.55—7.30 (m, 15 H, C_6H_5P) and 1.78 (s, 15 H, C_5Me_5)} (Found: C, 62.45; H, 5.10; N, 2.50. Calc. for $C_{31}H_{30}MoNO_3P$: C, 62.95; H, 5.10; N, 2.35%).

Crystals suitable for *X*-ray analysis of both compounds were obtained upon recrystallization from methanol-tetrahydrofuran (thf).

Table 2. Crystal data for complexes (**2**) and (**3**)[a]

	(**2**)	(**3**)
Formula	$C_{30}H_{30}MoN_3O_2P$	$C_{31}H_{30}MoNO_3P$
M	591.5	591.5
a/Å	8.625(2)	8.641(1)
b/Å	18.655(9)	18.547(3)
c/Å	17.573(5)	17.52(1)
β/°	92.29(2)	91.15(3)
U/Å^3	2 825.2	2 807.9
D_c/g cm^{-3}	1.39	1.40
F(000)	1 216	1 216
Purple-red crystals/mm	0.2 × 0.1 × 0.1	0.1 × 0.15 × 0.1
μ(Mo-K_α)/cm^{-1}	5.47	5.51
Scan interval/°	0.9 + 0.35 tanθ	1.3 + 0.35 tanθ
Prescan speed/° min^{-1}	9	6
No. of data collected at room temperature	5 501	5 341
No. of independent data [$I > 2.5\sigma(I)$]	3 315	2 045
Absorption correction range[b]	1.0—0.85	1.0—0.66
R	0.032	0.044
R′[c]	0.034	0.046

[a] Details of measurement common to both: monoclinic; $Z = 4$; space group $P2_1/c$; Mo-K_α (λ = 0.710 69 Å) radiation; Enraf-Nonius CAD-4 diffractometer; scan range $2.5 < \theta < 25°$, scan type ω—2θ; prescan acceptance $\sigma(I)/I = 0.5$, required $\sigma(I)/I = 0.01$ for measured reflections; background measurement equal to half the peak scanning time; maximum allowed scanning time 140 s; collected octants $\pm h,k,l$; equivalent reflections merging 0.01. [b] Ref. 19. [c] $R' = \Sigma|(F_o - F_c)w^{\frac{1}{2}}|/\Sigma(F_o w^{\frac{1}{2}})$ where $w = k/[\sigma^2(F) + |g|F^2]$ and k = 0.87 for (**2**) and 1.07 for (**3**) and g = 0.001 for (**2**) and 0.0015 for (**3**).

Table 3. Fractional atomic co-ordinates for complex (**2**)

Atom	*x*	*y*	*z*
Mo	0.813 66(3)	0.180 41(2)	0.621 08(2)
P	0.739 27(10)	0.312 49(5)	0.629 11(5)
C(1)	0.617 8(4)	0.181 3(2)	0.558 8(2)
O(1)	0.502 4(4)	0.175 7(2)	0.525 2(2)
C(2)	0.675 5(5)	0.122 3(2)	0.679 6(2)
O(2)	0.597 0(4)	0.084 1(2)	0.712 9(2)
N(1)	0.896 1(4)	0.210 9(2)	0.733 0(2)
N(2)	0.931 7(5)	0.187 3(2)	0.791 0(2)
N(3)	0.976 5(7)	0.165 6(3)	0.850 9(3)
C(3)	0.629 8(4)	0.336 1(2)	0.713 0(2)
C(4)	0.539 5(5)	0.285 1(2)	0.747 5(2)
C(5)	0.451 3(5)	0.302 8(3)	0.809 4(3)
C(6)	0.455 2(6)	0.370 5(3)	0.838 8(2)
C(7)	0.545 0(6)	0.421 6(2)	0.806 1(3)
C(8)	0.633 9(5)	0.405 1(2)	0.743 3(2)
C(9)	0.619 1(4)	0.346 8(2)	0.549 3(2)
C(10)	0.473 0(5)	0.376 4(2)	0.557 8(3)
C(11)	0.386 3(6)	0.399 1(3)	0.494 8(3)
C(12)	0.443 7(6)	0.394 3(3)	0.423 2(3)
C(13)	0.586 9(6)	0.364 7(3)	0.413 8(3)
C(14)	0.676 6(5)	0.341 3(2)	0.476 7(2)
C(15)	0.899 0(4)	0.377 8(2)	0.634 0(2)
C(16)	1.031 4(4)	0.362 9(2)	0.679 7(2)
C(17)	1.151 2(5)	0.412 1(3)	0.685 7(3)
C(18)	1.140 4(6)	0.476 3(3)	0.647 9(3)
C(19)	1.011 8(6)	0.491 8(3)	0.602 9(3)
C(20)	0.891 8(5)	0.442 4(2)	0.595 7(2)
C(21)	0.888 7(5)	0.086 6(2)	0.547 9(2)
C(22)	0.987 6(5)	0.088 0(2)	0.614 1(2)
C(23)	1.082 3(4)	0.149 7(3)	0.610 4(2)
C(24)	1.041 0(4)	0.188 9(2)	0.544 0(2)
C(25)	0.918 2(4)	0.149 7(2)	0.505 5(2)
C(26)	0.782 1(6)	0.025 6(2)	0.521 9(3)
C(27)	1.008 6(7)	0.028 2(3)	0.672 8(3)
C(28)	1.214 9(5)	0.169 1(3)	0.665 3(3)
C(29)	1.121 7(5)	0.253 6(3)	0.514 5(3)
C(30)	0.858 8(5)	0.165 5(2)	0.425 1(2)

Table 4. Fractional atomic co-ordinates for complex (**3**)

Atom	*x*	*y*	*z*
Mo	0.809 35(8)	0.177 97(4)	0.620 23(4)
P	0.737 8(2)	0.310 9(1)	0.629 4(1)
C(1)	0.616 3(9)	0.179 5(5)	0.560 6(5)
O(1)	0.502 6(7)	0.175 5(4)	0.524 2(4)
C(2)	0.668 5(10)	0.120 5(5)	0.678 5(5)
O(2)	0.587 0(9)	0.082 0(4)	0.712 2(4)
N	0.886 1(8)	0.204 7(4)	0.735 8(4)
C(3)	0.937 6(12)	0.188 0(5)	0.792 1(4)
O(3)	0.995 3(14)	0.172 6(6)	0.855 4(4)
C(4)	0.624 5(8)	0.334 0(5)	0.712 8(4)
C(5)	0.530 5(11)	0.283 9(5)	0.745 9(6)
C(6)	0.439 0(12)	0.299 7(6)	0.808 1(6)
C(7)	0.446 5(13)	0.366 8(7)	0.839 4(6)
C(8)	0.540 1(12)	0.418 4(6)	0.806 4(6)
C(9)	0.629 4(11)	0.403 1(5)	0.745 2(5)
C(10)	0.621 6(9)	0.345 6(4)	0.549 0(5)
C(11)	0.475 4(10)	0.376 0(5)	0.556 9(6)
C(12)	0.390 7(11)	0.397 8(6)	0.493 8(7)
C(13)	0.452 8(12)	0.393 6(6)	0.422 8(6)
C(14)	0.596 4(12)	0.363 6(5)	0.413 0(5)
C(15)	0.682 6(10)	0.339 9(5)	0.476 9(5)
C(16)	0.897 6(9)	0.376 8(4)	0.634 7(5)
C(17)	1.028 5(9)	0.360 8(5)	0.679 2(5)
C(18)	1.150 5(11)	0.409 2(6)	0.685 2(6)
C(19)	1.138 6(11)	0.474 7(6)	0.647 0(6)
C(20)	1.011 9(12)	0.490 6(5)	0.604 9(6)
C(21)	0.891 7(12)	0.441 7(5)	0.596 9(6)
C(22)	0.881 7(10)	0.084 3(5)	0.546 1(5)
C(23)	0.981 2(11)	0.085 3(5)	0.611 6(6)
C(24)	1.077 0(9)	0.146 3(5)	0.607 1(5)
C(25)	1.037 9(8)	0.186 1(5)	0.542 4(5)
C(26)	0.916 1(9)	0.147 9(5)	0.504 0(5)
C(27)	0.776 9(13)	0.024 3(5)	0.519 5(6)
C(28)	1.000 2(14)	0.023 9(6)	0.671 4(6)
C(29)	1.209 2(10)	0.163 5(7)	0.662 3(6)
C(30)	1.119 3(9)	0.251 2(5)	0.512 4(5)
C(31)	0.858 0(10)	0.164 2(5)	0.423 6(5)

Reaction of $[Mo(CO)_3(\eta\text{-}C_5Me_5)(PPh_3)]BF_4$ (**1**) *with* KNCO.—To a solution of complex (**1**) (0.127 g, 0.191 mmol) in methanol (15 cm^3) was added KNCO (15.5 mg, 0.191 mmol) and the mixture was warmed to 40 °C. After 2 d, solution i.r. spectra showed that the reaction was complete; the solution was cooled to -70 °C and the red crystals which precipitated were collected by filtration and vacuum dried (70% yield). Spectroscopic and analytical results were identical to those obtained for $[Mo(CO)_2(\eta\text{-}C_5Me_5)(PPh_3)(NCO)]$ prepared above.

Crystal Structure Determinations of Complexes (**2**) *and* (**3**).—Crystal data and details of measurements are reported in Table 2 for both complexes (**2**) and (**3**). The diffraction experiments were carried out at room temperature on an Enraf-Nonius CAD4 diffractometer with Mo-K_α radiation. The unit cell was determined from 25, randomly selected, high-θ, reflections. Data were reduced to F_o values and corrected for Lorentz polarization effects. Empirical absorption corrections were applied by the Walker and Stuart method[19] once complete structural models were obtained and all atoms refined isotropically. The structure of (**2**) was solved by the Patterson method, subsequent difference Fourier maps affording the positions of all light atoms. Co-ordinates from (**2**) were used as preliminary input in the refinement of (**3**) taking advantage of their isomorphism. Hydrogen atoms for the phenyl and methyl groups were added in calculated positions (C–H 1.08 Å) and their co-ordinates were refined 'riding' on the corresponding C atoms. No geometrical constraints were applied to the phenyl or C_5Me_5 groups. Thermal vibrations were treated anisotropically for all non-hydrogen atoms. Two individual isotropic values were refined for H(phenyl) and H(methyl) atoms [0.168(7), 0.104(3) for (**2**); 0.115(9), 0.098(9) $Å^2$ for (**3**)].

For all calculations the SHELX 76[20] package of crystallographic programs was used. A residual electron density peak of about 0.7 e $Å^{-3}$ was found in the final Fourier maps of (**3**) almost halfway from the N and C(3) atoms, at a distance of *ca.* 2.7 Å from the Mo atom. It was taken as indicative of the presence of disorder in the structure attributable to an unresolved small fraction of an atom pair, which could well belong to an O-bonded NCO group with the terminal N atom superimposed on the atom of the N-bonded group. Interestingly this disorder model is in keeping with the spectroscopic evidence mentioned above. However all attempts to refine the two images with combined occupancies failed to give meaningful results, probably because of the very low atomic fractions involved (site occupation factor <0.1 for the less populated image). Atomic co-ordinates are reported in Tables 3 and 4 for (**2**) and (**3**) respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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