Formation of the Molybdenum Metallacycle [Mo(η^5-C_5H_5)$_2${OC(O)N(Ph)}] from the Formal [2+2] Coupling of Phenyl Isocyanate with a Metal–Oxo Linkage

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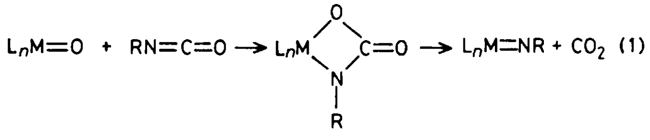
The oxo complex [Mo(η^5-C_5H_5)$_2$(O)] (**2**) reacts with PhNCO to form the structurally characterized cyclometallacarbamate [Mo(η^5-C_5H_5)$_2${OC(O)N(Ph)}] (**3**), derived from the formal [2 + 2] coupling of the C=N double bond of an isocyanate with a terminal metal–oxo linkage.

One of the more important and general methods for the synthesis of metal imido complexes (M=NR) involves the reaction of isocyanates with metal–oxo complexes.[1,2] This reaction has been suggested to proceed *via* the intermediacy of metallacycles such as (**1**), reaction (1),[3] although such species have rarely been observed.[3c] Here we report an example of the formal [2 + 2] cycloaddition of an isocyanate C=N bond to a metal–oxo linkage to give a cyclometallacarbamate of type (**1**).

Addition of PhNCO (1.0 ml, 9.2 mmol) to an emerald-green solution of [Mo(η-C_5H_5)$_2$(O)][4] (**2**) (0.25 g, 1.07 mmol) in dichloromethane (20 ml) led over 1.5 h to the formation of a dark orange–red solution. Removal of the solvent under reduced pressure followed by trituration with pentane (2 × 30 ml) gave [Mo(η-C_5H_5)$_2${OC(O)N(Ph)}] (**3**) as a tan powder contaminated with significant quantities of a mixture of phenyl isocyanate dimer and trimer, reaction (2).[5] The complex (**3**) was obtained pure as a dark orange, air-stable, microcrystalline solid (0.15 g, 0.48 mmol, 39%) by repeatedly solvating the tan powder in the minimum of CH_2Cl_2 (*ca.* 10 ml), filtering, and rapidly adding diethyl ether (*ca.* 100 ml), followed by recrystallization from a saturated solution in 1 : 1 acetone–octane under argon.†

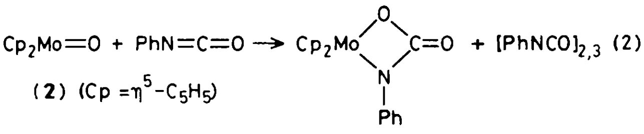
An *X*-ray diffraction study of (**3**) (Figure 1)‡ shows (within statistical error) a planar metallacycle as well as a planar co-ordination geometry about the nitrogen atom N(1). Both the N(1)–C(1) distance of 1.365(5) Å and the C(1)–O(2) distance of 1.334(6) Å are indicative of partial multiple bond character but are normal for N–C distances [1.36(3) Å] and C–O distances [1.33(3) Å] in structures containing the carbamate functionality.§ The Mo–N(1) and Mo–O(2) distances appear to represent normal single bonds, and the C(1)–O(1) distance of 1.225(6) Å is characteristic of a C=O double bond.



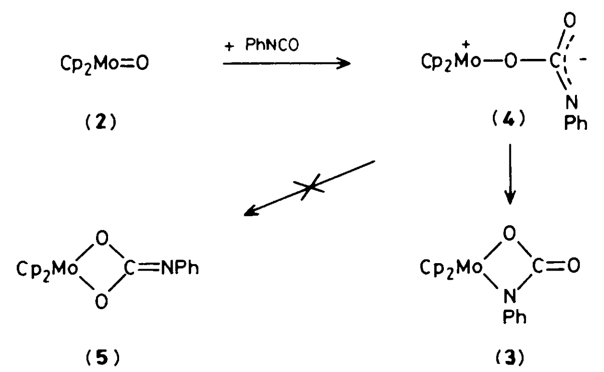
(**1**)

We suggest that the formation of (**3**) involves nucleophilic attack of the oxo ligand of (**2**) on the electrophilic carbon atom of the isocyanate to give the zwitterion (**4**) (Scheme 1). Ring closure *via* nitrogen addition to the metal to yield (**3**) rather than oxygen addition to form (**5**) may reflect the greater strength of C=O bonds relative to C=N bonds. The formation of phenyl isocyanate oligomers in reaction (2) can also be rationalized by the intermediacy of (**4**) since similar species have been proposed to be involved in the base-catalysed cyclization of isocyanates.[5] Alternatively (**3**) could form by a concerted [2 + 2] cycloaddition reaction.

The formation of (**3**) provides support for the suggested involvement of metallacycles of type (**1**) in the isocyanate to imido conversion.[3] However, the metallacyclic core within (**3**) has proved to be remarkably stable: all attempts to induce CO_2 loss to generate the imido complex [Mo(η^5-C_5H_5)$_2$(NPh)] by prolonged heating in various solvents (THF, reflux, 42 h; toluene, reflux, 17 h) met with failure. The complex (**3**) was recovered quantitatively from these reactions. An attempt at photochemically inducing the elimination [u.v., $(CD_3)_2CO$] resulted in rapid destruction of the complex. The oxo complex



(**3**)



Scheme 1

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† *Spectroscopic data* for (**3**): ^{1}H n.m.r. [200 MHz; $(CD_3)_2CO$] δ 7.35—6.65 (m, 5H, C_6H_5) and 5.58 (s, 10H, $2C_5H_5$); i.r. (KBr) 3110m, 3090m, 1626vs, 1588s, 1485s, 1449m, 1428m, 1372mw, 1335vs, 1285mw, 1225s, 1076m, 1019m, 994m, 905mw, 839ms, 797m, 756ms, 731m, 696m, 673m, 519mw, and 445mw cm^{-1}.

‡ Dark orange-red parallelopipeds suitable for *X*-ray analysis were obtained by acetone/ether layer diffusion. *Crystal data* for (**3**): $C_{17}H_{15}NO_2Mo$, $M = 361.3$, monoclinic, space group $P2_1/c$, $a = 13.534(2)$, $b = 7.4063(8)$, $c = 14.448(3)$ Å, $\beta = 99.955(9)°$, $U = 1426.3(4)$ Å^3, $Z = 4$, $D_c = 1.68$ g cm^{-3}, μ(Mo-K_α) = 9.1 cm^{-1}. A Nicolet R3m/μ diffractometer was used to collect 4618 reflections ($4° \leqslant 2\theta \leqslant 60°$) of which 4156 were unique and 3097 with $F_o \geqslant 5\sigma(F_o)$ were considered observed. The Mo atom was located by heavy-atom methods. All remaining atoms were located from subsequent difference Fourier syntheses. Non-hydrogen atoms were refined anisotropically. At convergence $R = 5.47$, $R_w = 5.79$, goodness of fit 1.226, $(\Delta/\sigma) = 0.027$, $\Delta(\rho) = 1.38$ e Å^{-3} (near Mo), $N_o/N_v = 12.3$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Values cited are mean values obtained from the Cambridge Crystallographic Database for all structures containing the carbamate moiety.

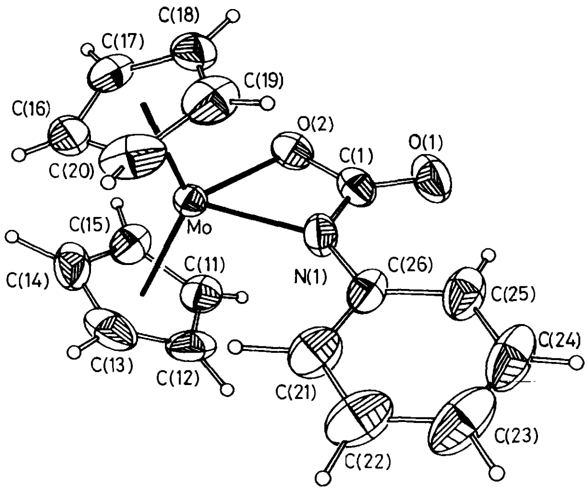

Figure 1. Molecular structure and labelling scheme for (**3**). Mo–Cp(1), 1.983(6); Mo–Cp(2), 1.977(6); Mo–N(1), 2.105(4); Mo–O(2), 2.103(3); O(1)–C(1), 1.225(6); O(2)–C(1), 1.334(6); N(1)–C(1), 1.365(5); N(1)–C(26), 1.401(6); O(2)–Mo–N(1), 61.9(1); O(2)–Mo–Cp(1), 109.4(2); N(1)–Mo–Cp(1), 108.9(2); O(2)–Mo–Cp(2), 106.3(2); N(1)–Mo–Cp(2), 106.3(2); Cp(1)–Mo–Cp(2), 136.6(2); Mo–O(2)–C(1), 96.3(2); Mo–N(1)–C(1), 95.2(3); Mo–N(1)–C(26), 137.9(3); C(1)–N(1)–C(26), 126.9(4); O(1)–C(1)–O(2), 124.3(4); O(1)–C(1)–N(1), 129.1(5); O(2)–C(1)–N(1), 106.6(4) [Cp(1) = ring centroid of C(11)C(12)C(13)C(14)C(15); Cp(2) = ring centroid of C(16)C(17)C(18)C(19)C(20)].

[$Mo(\eta^5-C_5H_5)_2(O)$] also reacts with other heteroallenes (MeNCO, PhNCS, CS_2, $PhCH_2N_3$, and PhNSO), but these reactions are not as clean as reaction (2), and the products have yet to be characterized.

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