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An Allylimido Complex of Molybdenum(V): Preparation and Structure of *cis,mer*-[CH_2═$CHCH_2N$≡$MoCl_3(OPPh_3)_2$]

Yuhua Du,[†] Arnold L. Rheingold,[‡] and Eric A. Maatta*,[†]

Departments of Chemistry, Kansas State University,
Manhattan, Kansas 66506-3701, and
University of Delaware, Newark, Delaware 19716

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The solution chemistry of high-valent group VI complexes containing allylimido,[1,2] allylamido,[3] and allyloxo[3] ligands has received attention in attempts to reproduce various species and reaction pathways thought to be involved in the heterogeneous catalytic oxidation and ammoxidation of propylene.[4] In this contribution, we describe the preparation and structure of an allylimido Mo(V) complex, [CH═$CHCH_2N$≡$MoCl_3(OPPh_3)_2$], **2**, in which the allylimido ligand framework is more precisely delineated than in our previous work.[1b]

Table 1. Crystallographic Data for [CH_2═$CHCH_2N$≡$MoCl_3(OPPh_3)_2$]·$0.5CH_2Cl_2$

formula	$C_{39.5}H_{36}NO_2P_2Cl_4Mo$
fw[a]	856.4
cryst dimens, mm³	0.46 × 0.57 × 0.58
cryst color	dark green
cryst system	orthorhombic
space group	*Pbca* (No. 61)
a, Å	19.999(6)
b, Å	12.538(3)
c, Å	33.851(7)
V, Å³	8488.3(41)
Z	8
D(calc),[a] g cm⁻³	1.34
μ(Mo Kα), cm⁻¹	6.0
temp, °C	23
radiation (λ, Å)	Mo Kα (0.710 73)
R(*F*), %[b]	6.45
$R_w(F)$, %[b]	6.66

[a] Molecular weight and density calculated with 0.5 molecule of CH_2Cl_2. [b] $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Experimental Section

Preparation of [CH_2═$CHCH_2N$≡$MoCl_3(OPPh_3)_2$], 2. A nitrogen-blanketed suspension of [$MoCl_4(THF)_2$] (2.0 g; 5.24 mmol) in 80 mL of dry CH_2Cl_2 at room temperature was treated with allyl azide[5] (0.44 g; 5.24 mmol). After 30 min of stirring, $OPPh_3$ (2.92 g; 10.5 mmol) was added. After a further 30 min, the green solution was reduced to *ca.* 50% of its original volume by evaporation, and approximately 50 mL of diethyl ether were introduced. Large green crystalline cubes of the hemisolvate **2**·0.5 CH_2Cl_2 formed within several hours (3.7 g; 82.4% yield). Anal. Calcd (found) for vacuum-dried **2**·0.5 CH_2Cl_2, $C_{39.5}H_{36}NO_2P_2Cl_4Mo$: C, 55.40 (55.49); H, 4.24 (4.09); N, 1.63 (1.59). IR (Nujol, cm⁻¹): 1582 (m), 1432 (s), 1309 (m), 1260 (m), 1165 (s), 1135 (s), 1115 (s), 1082 (s), 1025 (s), 995 (s), 922 (s), 751 (s), 725 (s), 692 (s).

Table 2. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³)

	x	*y*	*z*	*U*
Mo	164.1(4)	5720.6(6)	6144.4(2)	40.9(2)[a]
Cl(1)	1039(1)	5414(2)	5669(1)	58(1)[a]
Cl(2)	181(2)	3907(2)	6349(1)	65(1)[a]
Cl(3)	−529(2)	6226(2)	6693(1)	76(1)[a]
P(1)	1446(1)	6185(1)	6883(1)	43(1)[a]
P(2)	280(1)	8232(2)	5750(1)	39(1)[a]
O(1)	973(3)	5970(4)	6552(2)	48(2)[a]
O(2)	303(3)	7360(4)	6053(2)	46(2)[a]
N	−474(4)	5542(6)	5818(2)	57(3)[a]
C(1)	−989(7)	5304(11)	5546(4)	114(7)[a]
C(2)	−1351(7)	4327(14)	5629(6)	149(9)[a]
C(3)	−1687(12)	3709(22)	5378(7)	237(16)[a]
C(11)	2701(4)	7107(5)	6851(2)	78(5)[a]
C(12)	3339	7237	6691	96(6)[a]
C(13)	3542	6608	6374	70(4)[a]
C(14)	3108	5849	6215	71(4)[a]
C(15)	2470	5720	6375	56(3)[a]
C(16)	2266	6349	6693	47(3)[a]
C(21)	2041(3)	4814(6)	7427(2)	72(4)[a]
C(22)	2033	3961	7691	79(5)[a]
C(23)	1442	3395	7755	76(5)[a]
C(24)	860	3682	7554	69(4)[a]
C(25)	869	4535	7290	58(4)[a]
C(26)	1459	5101	7226	46(3)[a]
C(31)	1159(4)	7398(5)	7555(2)	77(5)[a]
C(32)	1026	8357	7749	90(5)[a]
C(33)	970	9301	7533	83(5)[a]
C(34)	1046	9286	7124	98(6)[a]
C(35)	1178	8327	6930	95(6)[a]
C(36)	1235	7383	7146	49(3)[a]
C(41)	1215(3)	9108(5)	5232(2)	60(4)[a]
C(42)	1868	9337	5115	71(4)[a]
C(43)	2406	8957	5337	77(5)[a]
C(44)	2290	8349	5675	72(5)[a]
C(45)	1636	8120	5792	53(4)[a]
C(46)	1099	8500	5570	40(3)[a]
C(51)	−867(3)	8283(5)	5281(2)	71(4)[a]
C(52)	−1245	7981	4953	88(5)[a]
C(53)	−970	7306	4669	74(5)[a]
C(54)	−317	6932	4712	73(5)[a]
C(55)	61	7234	5040	58(4)[a]
C(56)	−214	7910	5325	46(3)[a]
C(61)	−323(4)	9293(5)	6353(2)	105(6)[a]
C(62)	−602	10178	6541	146(9)[a]
C(63)	−617	11162	6349	97(6)[a]
C(64)	−354	11262	5969	73(5)[a]
C(65)	−76	10377	5781	62(4)[a]
C(66)	−60	9392	5973	47(3)[a]
Cs(1)	−2601(8)	6626(12)	6702(4)	118(5)[b]
Cs(2)	−2274(32)	6199(56)	6218(18)	263(28)[b]
Cs(3)	−2492(14)	6525(22)	5812(8)	93(8)[b]
Cs(4)	−2097(25)	7699(41)	6102(14)	209(21)[b]
Cs(5)	−2381(18)	5962(28)	6659(10)	133(12)[b]
Cs(6)	−2449(24)	7251(41)	6354(13)	205(19)[b]
Cs(7)	−2720(35)	5336(53)	6030(19)	298(32)[b]

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Carbon atoms labeled Cs are found in the highly disordered CH_2Cl_2 molecule.

X-ray Crystallography for 2·0.5 CH_2Cl_2. A suitable crystal was mounted on a glass fiber with epoxy cement. Crystal, data collection, and refinement parameters are collected in Table 1. The unit-cell parameters were obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). The systematic absences in the diffraction data

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[†] Kansas State University.

[‡] University of Delaware.

(1) (a) Maatta, E. A.; Du, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8249. (b) Maatta, E. A.; Du, Y.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1990**, 756. (c) Du, Y.; Rheingold, A. L.; Maatta, E. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2163.

(2) Forster, G. D.; Hogarth, G. *J. Organomet. Chem.* **1994**, *471*, 161.

(3) (a) Belagem, J.; Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 1501. (b) Belagem, J.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1993**, 1125. (c) Belagem, J.; Kress, J.; Osborn, J. A. *J. Mol. Catal.* **1994**, *86*, 267.

(4) For a summary of the extensive mechanistic studies of these reactions, see the following and references therein: Grasselli, R. K.; Burrington, J. D. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 394.

(5) Priebe, H. *Acta Chem. Scand., Ser. B* **1984**, *38*, 895.

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Table 3. Selected Bond Distances (Å) and Angles (deg) for $[CH_2{=}CHCH_2{\equiv}MoCl_3(OPPh_3)_2]{\cdot}0.5CH_2Cl_2$

	Distances		
Mo−N	1.703(8)	Mo−O(2)	2.097(6)
Mo−Cl(1)	2.407(3)	N−C(1)	1.41(2)
Mo−Cl(2)	2.378(3)	C(1)−C(2)	1.45(2)
Mo−Cl(3)	2.403(3)	C(2)−C(3)	1.33(3)
Mo−O(1)	2.151(6)		
	Angles		
N−Mo−O(1)	179.1(3)	O(2)−Mo−Cl(1)	87.8(2)
N−Mo−O(2)	97.6(3)	O(2)−Mo−Cl(2)	168.1(2)
N−Mo−Cl(1)	95.2(3)	O(2)−Mo−Cl(3)	86.2(2)
N−Mo−Cl(2)	94.2(3)	Cl(1)−Mo−Cl(2)	91.8(1)
N−Mo−Cl(3)	96.0(3)	Cl(1)−Mo−Cl(3)	167.9(1)
O(1)−Mo−O(2)	81.5(2)	Cl(2)−Mo−Cl(3)	92.0(1)
O(1)−Mo−Cl(1)	84.6(2)	Mo−N−Cl(1)	175.3(8)
O(1)−Mo−Cl(2)	86.6(2)	N−C(1)−C(2)	115(1)
O(1)−Mo−Cl(3)	84.2(2)	C(1)−C(2)−C(3)	128(2)
Mo−O(1)−P(1)	170.6(4)	Mo−O(2)−P(2)	144.3(4)

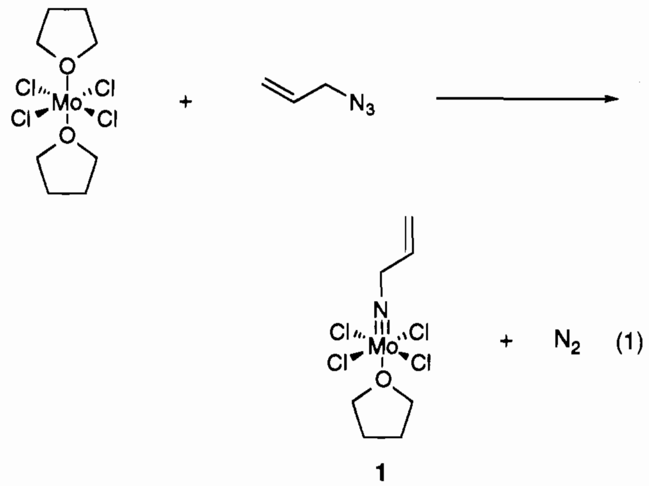
uniquely established the space group as *Pbca*. No correction for absorption was applied (low μ).

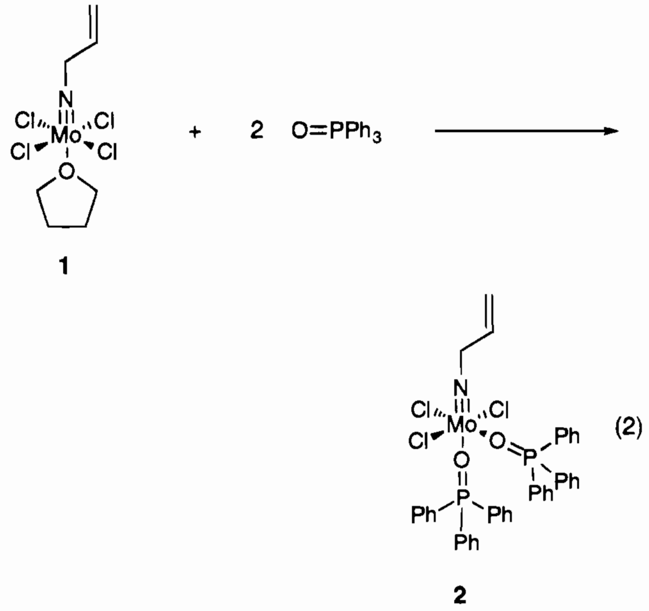
The structure was solved using a Patterson projection which located the Mo atom. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions (d_{CH} = 0.960 Å; U = 1.2U(for attached C)). A highly disordered small molecule found remotely positioned from other species in the structure, and unable to be identified from the crystallographic data, is likely to be one of the recrystallization solvents, CH_2Cl_2 (s.o.f. = 0.5) or Et_2O (s.o.f. = 1.0). Models based on these solvents and occupancy factors refined to identical R factors. Elemental analysis data agree better with the formulation **2**·0.5 CH_2Cl_2. As no discernible chemical interpretation could be given to the positions of the atoms (Cs(1)−Cs(7)) in relation to either solvent, the positions were assigned C atom identities and were refined with occupancies that produced thermal parameters in keeping with the overall thermal activity of the structure. With the exception of the atoms of the badly disordered solvent molecule, all non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl groups were constrained as rigid rings. Positional parameters are collected in Table 2, and selected bond distances and angles are listed in Table 3. All software and the sources of the scattering factors are contained in the SHELXTL(5.1) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Hydrolysis of 2. A solution of **2** in CH_2Cl_2 was allowed to stand open to the atmosphere overnight, causing the deposition of pale green transparent crystals of $[O{\equiv}MoCl_3(OPPh_3)_2]$, **3**, which were collected by filtration and dried under vacuum. Anal. Calcd (found) for $C_{36}H_{30}O_3P_2Cl_3Mo$: C, 55.80 (55.47); H, 3.90 (4.18). IR (Nujol, cm^{-1}): 970 (s), υ(Mo≡O) (lit.[6] 967).

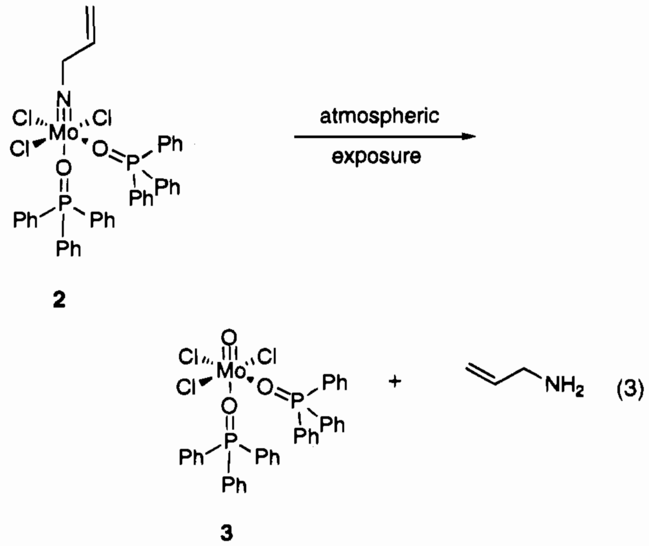
Results and Discussion

Preparation and Hydrolysis of 2. Allyl azide efficiently oxidizes $[MoCl_4(THF)_2]$ to afford the unstable Mo(VI) allylimido complex $[CH_2{=}CHCH_2N{\equiv}MoCl_4(THF)]$, **1**, as shown in eq 1.[1b] Addition of 2 equiv of triphenylphosphine oxide to a CH_2Cl_2 solution of **1** induces substitution and reduction at the Mo center, producing the allylimido Mo(V) species $[CH_2{=}CHCH_2N{\equiv}MoCl_3(OPPh_3)_2]$, **2**, in high yield (eq 2). Formation of **2** from **1** in this manner requires the formal loss of a chlorine atom, whose fate has not been determined. The instability of **1** toward the O=PPh$_3$ nucleophile may be contrasted with the behavior of its W(VI) analogue, which forms a stable OPPh$_3$ complex, $[CH_2{=}CHCH_2N{\equiv}WCl_4(OPPh_3)]$.[7] This disparity accords with established general trends in the ease of reduction among high-valent group VI metals.





Upon exposure to the atmosphere, CH_2Cl_2 solutions of **2** deposit pale green crystals of the oxo−Mo(V) hydrolysis product $[O{\equiv}MoCl_3(OPPh_3)_2]$, **3**, as shown in eq 3. We presume that



in this process the allylimido group within **2** is liberated as allylamine, but we did not attempt to confirm its presence. **3** has been prepared previously from the reaction of $MoCl_5$ with

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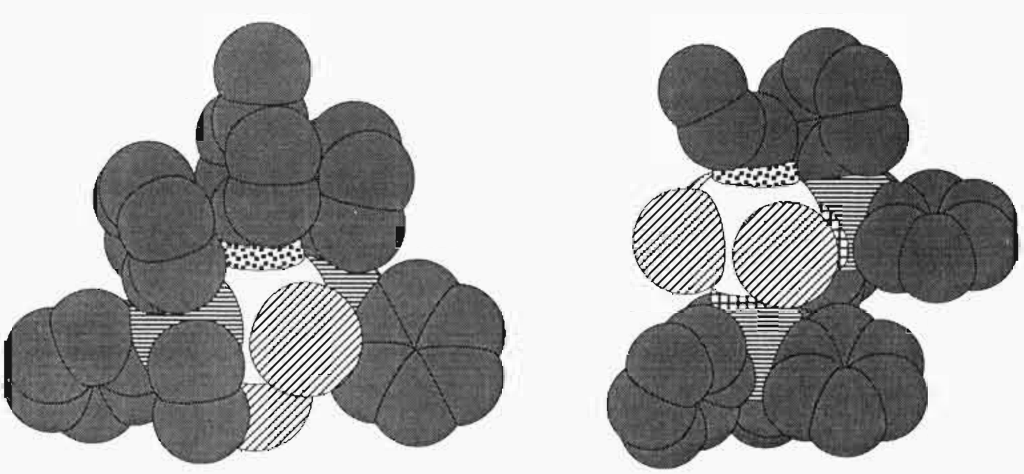
(6) Horner, S. M.; Tyree, S. Y., Jr. *Inorg. Chem.* **1962**, *1*, 122.

(7) Du, Y.; Maatta, E. A. Unpublished observations.

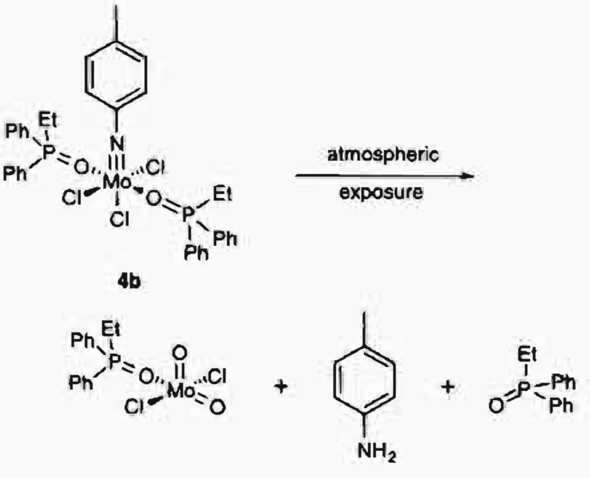


4a 2

Figure 1. Space-filling representations of the structures of *trans,mer*-[$CH_3C_6H_4N{\equiv}MoCl_3(PEtPh_2)_2$] (**4a**)[9] and *cis,mer*-[$CH_2{=}CHCH_2N{\equiv}MoCl_3(OPPh_3)_2$] (**2**). *The imido nitrogen atoms are speckled.*

$OPPh_3$ in ethanol,[6] and it is known to display *cis,mer*-geometry on the basis of an X-ray crystallographic study.[8]

The simple hydrolytic reactivity observed for **2** upon air exposure differs from that displayed by the related *p*-tolylimido-Mo(V) systems *trans,mer*-[$CH_3C_6H_4N{\equiv}MoCl_3L_2$], **4** (**4a**, L = $PEtPh_2$; **4b**, L = $OPEtPh_2$).[9] For **4a** and **4b**, atmospheric exposure results in both oxidation and hydrolysis producing the dioxo-Mo(VI) product [$MoO_2Cl_2(OPEtPh_2)$] *via* the presumed intermediacy of [$MoO(Ntol)Cl_2L_2$], along with *p*-toluidine and free $OPEtPh_2$ (eq 4). A plausible explanation for the different reactivities observed for the allylimido- and *p*-tolylimido-Mo(V) systems involves the relative accessibilities of the imido nitrogen atom vs the Mo center as reactive sites (Figure 1). In the *trans,mer*-geometry of complexes **4**, the imido nitrogen atom resides in the rather shielded pocket formed by the phosphine or phosphine oxide ligands. Complexes **4** are inert to H_2O, and for these systems, the primary reaction event upon exposure to the atmosphere involves reaction of O_2 at the Mo atom; hydrolysis of the tolylimido ligand occurs only after oxidation to the Mo(VI) state. For **2**, the imido nitrogen atom is much more exposed and reaction with H_2O is thereby facilitated.



(4)

Molecular Structure of 2. An ORTEP view of **2** is shown in Figure 2. The pseudooctahedral coordination sphere contains a meridional arrangement of the three chlorine atoms and a *cis* disposition of the two triphenylphosphine oxide ligands, leading to virtual C_s local symmetry about the Mo atom. The allylimido ligand displays metrical parameters (Table 3) typical of triply-bonded imido species with a short Mo−N distance of 1.703(8) Å and an Mo−N−C(1) angle of 175.3(8)°. Distances and angles within the allyl substituent are in the expected ranges, despite some swelling of the thermal ellipsoids for C(2) and C(3). As has been observed previously,[9] the imido ligand in this d^1-system exerts a modest *trans*-influence of *ca.* 0.05 Å (Mo−O(1) = 2.151(6) Å; Mo−O(2) = 2.097(6) Å). The bond to the unique chloride ligand Cl(2) is approximately 0.03 Å shorter than those involving the pair of mutually *trans* chlorides. The two triphenylphosphine oxide ligands are bound to Mo in decidedly different fashions as revealed by the the Mo−O−P angles: Mo−O(1)−P(1) = 170.6(4)° and Mo−O(2)−P(2) = 144.3(4)°. Despite these angular variations, the two P−O bond

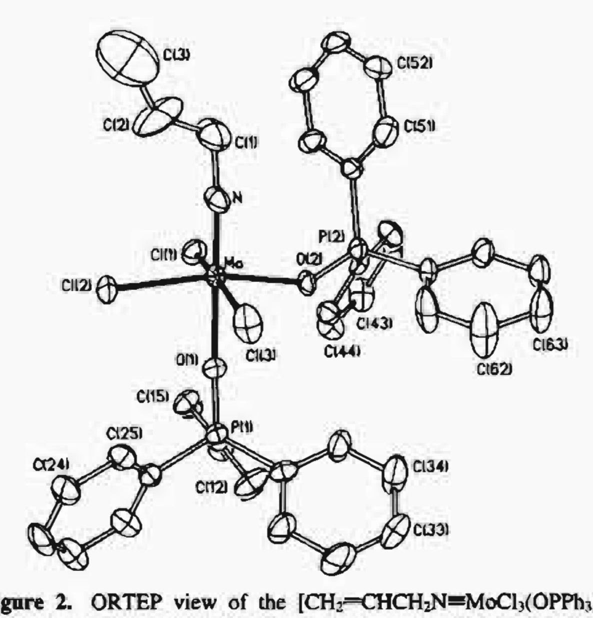


Figure 2. ORTEP view of the [$CH_2{=}CHCH_2N{\equiv}MoCl_3(OPPh_3)_2$] molecule in crystals of **2**·$0.5CH_2Cl_2$. Hydrogen atoms and the disordered solvent molecule have been omitted for clarity.

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(8) Garner, C. D.; Howlander, N. C.; Mabbs, F. E.; McPhail, A. T.; Onan, K. D. *J. Chem. Soc., Dalton Trans.* **1978**, 1848.

(9) The presence of the *trans,mer*-configuration has been verified by X-ray crystallography for [$CH_3C_6H_4N{\equiv}MoCl_3(PEtPh_2)_2$] and has been inferred, on the basis of comparative ESR studies, for [$CH_3C_6H_4N{\equiv}MoCl_3(OPEtPh_2)_2$]: Chou, C. Y.; Huffman, J. C.; Maatta, E. A. *Inorg. Chem.* **1986**, *25*, 822.

lengths are essentially identical (O(1)−P(1) = 1.489(6) Å; O(2)−P(2) = 1.500(6) Å). A similar arrangement was found in the structure of the analogous oxo complex **3**, in which the two Mo−O−P angles involving the triphenylphosphine oxide ligands are 168.6(7) and 145.6(7)°.[8] Other structural features of **3**, including the *trans*-influence exerted by the oxo ligand (0.07 Å) and the shortening of the unique Mo−Cl bond (0.035 Å), mirror the corresponding aspects noted above for **2**.

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Supplementary Material Available: Tables of crystallographic data, bond lengths, bond angles, anisotropic thermal parameters, and H atom coordinates and isotropic thermal parameters (5 pages). Ordering information is given on any current masthead page.

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