Crystal and Molecular Structure of a Dioxo-molybdenum Phosphorus-substituted Alkylidene resulting from the First Observed Aryl Migration from Molybdenum to Carbon

Henri Arzoumanian, André Baldy, Richard Lai,* Jacques Metzger, Marie-Louise Nkeng Peh, and Marcel Pierrot

I.P.S.O.I., Faculté des Sciences/Saint Jérôme, L.A. 126 du CNRS, Université Aix-Marseille III, 13013, Marseille, France

The reaction of $Mo(O)_2(mesityl)_2$ with Bu_3PCH_2 yields $(mesityl)(O)_2Mo=C(mesityl)PBu_3$, the first example of a dioxo-metal phosphorus-substituted carbene resulting from a double α-hydrogen abstraction and aryl migration from molybdenum to carbon within the co-ordination sphere of the metal.

Several recent reports published on the catalytic metathesis reaction of olefins indicate that high-valent transition metal oxo-alkylidene species certainly play a most important role as active catalytic intermediates in this process.[1] However, except for complexes of the type $W(O)(CHCMe_3)X_2$-$(PR_3)_2$,[1a,2,3] there is neither a general nor a direct synthetic route to this type of very important organometallic complexes.

Since a metal oxo-group M=O, can sometimes show ketone-like behaviour,[4] we decided to check whether a Wittig-type reaction is feasible between a metal oxo-complex and a phosphonium ylide $(R_3P=CR_2)$.
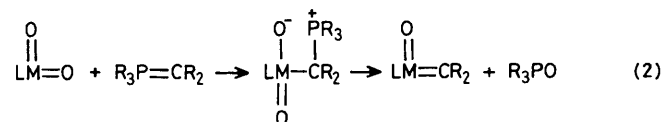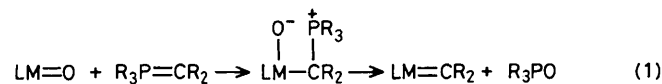
This type of reaction should provide a general route to a large variety of, either alkylidene, or, oxo-alkylidene complexes (equations 1 and 2).

During the course of this study[5] we obtained results showing a novel and unexpected reactivity of a dioxomolybdenum complex with methylenetributylphosphorane.

When $Mo(O)_2(mesityl)_2$[6] (mesityl $=$ 2,4,6-$C_6H_2Me_3$) (1 mol) was treated with Bu_3PCH_2 (2 mol) at 20 °C in pyridine, after evaporation of the solvent and removal of Bu_3PO by extraction into pentane, a residual oily brown material was obtained from which yellow–brown moderately air-sensitive crystals were obtained by crystallisation from a toluene–pentane mixture (10—15% yield). Besides peaks assigned to

n-butyl substituents and to mesityl groups, the $^{13}C\{^1H\}$ n.m.r. spectrum of these crystals in C_6D_6 exhibited one peak at δ 174 which was found to be a quaternary carbon atom by n.m.r. DEPT sequence. The $^{31}P\{^1H\}$ n.m.r. spectrum in C_6D_6 showed one peak at 16.7 p.p.m. The X-ray structure of these crystals revealed it as $(mesityl)(O)_2Mo=C(mesityl)PBu_3$ (1),† the first dioxo phosphorus-substituted carbene of molybdenum to be described. The molecular geometry of (1) is illustrated in Figure 1.

$$LM{=}O + R_3P{=}CR_2 \longrightarrow LM{-}\overset{\overset{+}{\overset{|}{P}R_3}}{\underset{|}{\overset{O^-}{C}}R_2} \longrightarrow LM{=}CR_2 + R_3PO \qquad (1)$$

$$\overset{O}{\underset{\|}{L}}M{=}O + R_3P{=}CR_2 \longrightarrow \overset{O^-\ \overset{+}{P}R_3}{\underset{\underset{O}{\|}}{LM{-}\underset{|}{C}R_2}} \longrightarrow \overset{O}{\underset{\|}{L}}M{=}CR_2 + R_3PO \qquad (2)$$
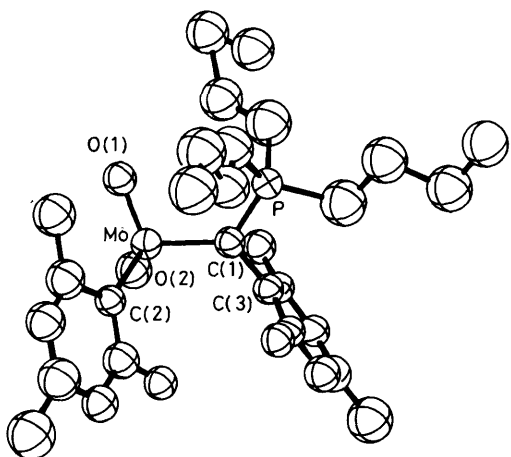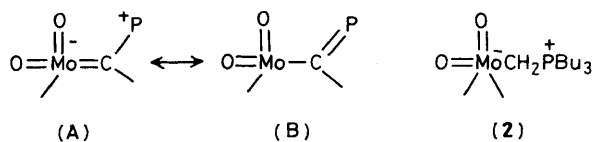
Figure 1. An ORTEP view of the geometry of the (mesityl)-(O)$_2$Mo=C(mesityl)PBu$_3$ molecule (**1**). Selected distances (mean values from the two independent molecules and variation from average values): Mo–O(1) 1.69(2), Mo–O(2) 1.68(2), Mo–C(1) 1.95(1), Mo–C(2) 2.15(5), C(1)–C(3) 1.50(5), P–C(1) 1.75(2), P–C(Bu) 1.80(5) Å; angles: O(1)–Mo–O(2) 114(1), C(1)–Mo–C(2) 105.5 (5), Mo–C(1)–C(3) 121(1), C(3)–C(1)–P 114.5(1.5), Mo–C(1)–P 125.5(1.5)°.

The angle values about C(1), as well as the Mo–C(1) bond length [1.95(1) Å], clearly indicate the sp^2 character of this carbon atom which is almost coplanar with Mo, P, and C(3) of the mesityl substituent. Both Mo–O(1) and Mo–O(2) distances, respectively 1.68(2) and 1.69(2) Å, lie in the range one would expect for a Mo=O bond [i.r. (Nujol mull) ν (Mo=O): 920 and 940 cm^{-1}]. These distances are comparable to the 1.661(11) Å value for W=O in W(O)(CHC-Me$_3$)(PEt$_3$)Cl$_2$.[1b] The Mo–mesityl, C(1)–mesityl, as well as P–n-Bu linkages are normal Mo–C(2) = 2.15(5), C(1)–(3) = 1.50(5), P–n-Bu = 1.80(5) Å, within the experimental errors. The Mo–C(1) distance, although similar to those generally found for carbenic complexes, is slightly longer than the W=C < double bond distance of 1.882(14) Å for W(O)(CHC-Me$_3$)(PEt$_3$)Cl$_2$.[1b] The Mo–C(1) distance of 1.95(1) Å is well in accord with some multiple bond character; on the other hand the P–C(1) distance of 1.75(2) Å lies in between a single (1.85 Å) and a double bond (1.66 Å).[7] These considerations coupled with the n.m.r. values of δ 174 for C(1), higher than expected for a true Mo=C <,[8] and 16.7 p.p.m. for P, far downfield for an ylide-like structure,[9] suggests a hybrid of the mesomeric forms (A) and (B), with predominance of the carbene-like form.

One question remained as to why the C(1) signal did not obviously split into a doublet: this observation although unexpected is not unprecedented.[10]

This new phosphinomethylidene complex is the first example of a molybdenum(vi) compound bearing two oxo-groups and a carbenic linkage. Moreover, its formation is also noteworthy since, in transition metal-ylide chemistry,[11] it constitutes the first occurrence of a double hydrogen atom abstraction from a methylene attached to a metal and, above all, it represents the only example showing unambiguously the migration of an aryl group from molybdenum to carbon within the co-ordination sphere.

Although the overall mechanism of the formation of (**1**) is not fully understood it, most certainly, goes through nucleophilic attack of Bu$_3$PCH$_2$ on the molybdenum atom to give an adduct such as (**2**). This adduct could then undergo a transylidation reaction losing H$^+$‡ followed by a second hydrogen loss which must occur as a hydride abstraction. Depending on whether the mesityl migration occurs before, or after, the second H abstraction, this process can be regarded as a phosphinomethylidene or a phosphinomethylidyne migratory insertion into a molybdenum–mesityl bond. Such a migration of alkyl[12] and phenyl[12b,13] groups to an alkylidene ligand bound to a transition metal atom has previously been suggested to rationalize reaction products.

The results reported here could have implications in the understanding of the key step in chain growth in many catalytic processes. Indeed, the importance of such metal complexes containing both organic and oxo-groups has recently been pointed out.[14]

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‡ The cation (Bu$_3$PCH$_3$)$^+$ is unambiguously characterized by its ^{13}C and ^{31}P n.m.r. spectra (C$_5$D$_5$N). ^{13}C{^{1}H} n.m.r., δ 24.16—23.7 [m, CH$_3$(CH$_2$)$_2$], 20.60 (d, J_{CP} 49 Hz, CH$_2$P), 13.5 [s, CH$_3$(CH$_2$)$_3$], 4.81 (d, J_{CP} 51 Hz, CH$_3$P); ^{31}P{^{1}H} n.m.r. 31.0 (s) p.p.m.