Synthesis and *X*-Ray Analysis of the First Example of a Phosphonium Ylide Complex of Dioxomolybdenum(VI)

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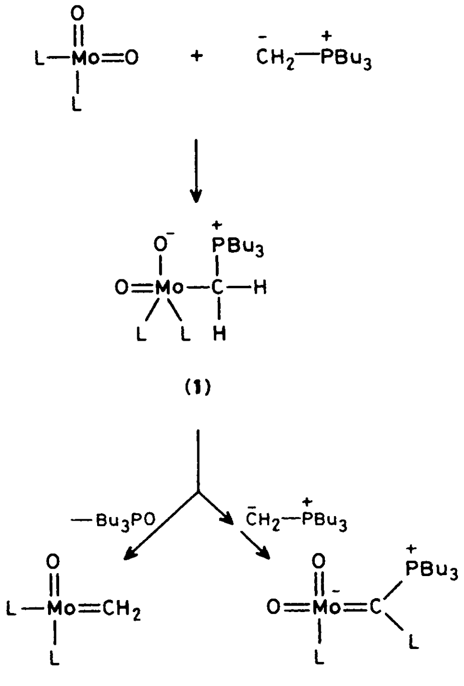
Addition of an equimolecular amount of $Bu_3P{=}CH_2$ to $Mo(O)_2(mesityl)_2$ in tetrahydrofuran yields the air-stable $(mesityl)_2Mo^-(O)_2CH_2P^+Bu_3$, the first example of a phosphonium dioxomolybdenum(VI) ylide complex; its structure has been determined by *X*-ray analysis.

In our search to find a general route to high oxidation state oxo-alkylidene transition metal complexes postulated as important intermediates in several catalytic reactions[1] we recently proposed a Wittig-type reaction between dioxo complexes and phosphorus ylides.[1] Preliminary results obtained with methylenetrialkylphosphoranes and $Mo(O)_2(mesityl)_2$ (mesityl = 2,4,6-$Me_3C_6H_2$) allowed the isolation and characterization of a dioxo phosphorus-substituted carbene of molybenum (**2**)[1] as well as the production of substantial amounts of Bu_3PO. This latter observation implicated strongly the formation of a mono-oxo-alkylidene complex (**3**) as is shown in Scheme 1. It further suggested the intermediacy of an adduct (**1**) analogous to a betaine in a classical organic Wittig reaction.

We have isolated and fully characterized this compound in the following way. Treatment of dioxo(dimesityl)molybdenum, in tetrahydrofuran (THF) at 0 °C, with Bu_3PCH_2 (1 equiv.) led to an almost instantaneous reaction as shown by a change in colour of the solution from yellow to orange-brown. Crystallization at 0 °C, from THF–pentane, of the orange-



Scheme 1. L = 2,4,6-$Me_3C_6H_2$.

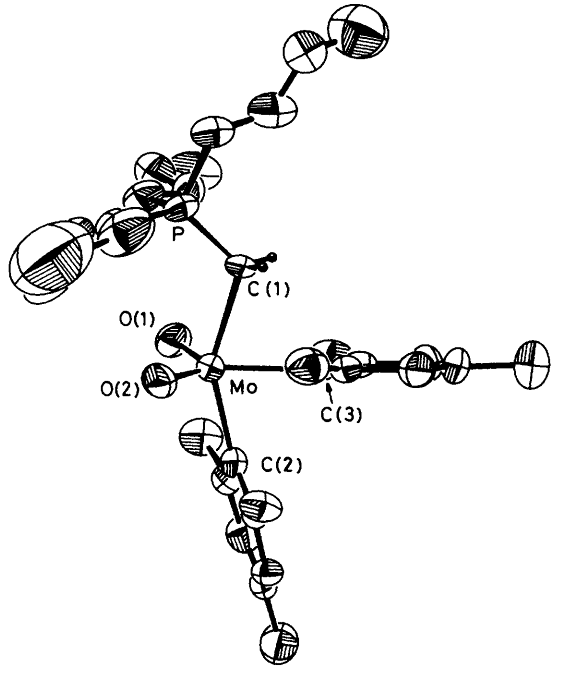
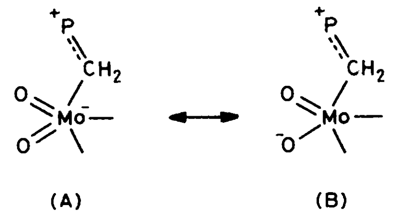


Figure 1. An ORTEP view of the $(mesityl)_2Mo(O)_2CH_2PBu_3$ molecule (**1**). Bond distances: Mo–O(1) 1.688(5), Mo–O(2) 1.706(5), Mo–C(1) 2.249(7), Mo–C(2) 2.224(6), Mo–C(3) 2.227(7), P–C(1) 1.765(7), P–C(Bu) 1.782(8) Å; bond angles: O(1)–Mo–O(2) 113.5(3), C(1)–Mo–C(2) 151.0(2), C(1)–Mo–C(3) 72.5(2), C(2)–Mo–C(3) 80.7(2), O(1)–Mo–C(3) 118.1(3), O(2)–Mo–C(3) 127.1(3), O(1)–Mo–C(2) 102.6(2), O(2)–Mo–C(2) 99.1(2)°.

yellow residue obtained after removal of THF *in vacuo* and pentane washings, yielded yellow crystals (60—65% yield).

The structure, as determined by *X*-ray diffraction, is shown in Figure 1.† The geometry around molybdenum is a distorted trigonal bipyramid with the two oxo groups and one mesityl ligand in the same plane, the molybdenum atom lying 0.12 Å below that plane. The Mo–C(1) bond length is 2.249(7) Å whereas the P–C(1) distance is 1.765(7) Å, showing some ylidic character for the P–C bond.[2]‡ The distances 1.688(5) and 1.706(5) Å for both Mo–O bonds lie in the range of Mo=O bonds.[3] The bond length difference between Mo–O(1) and Mo–O(2) is not significant enough to account for greater electron density on O(2). All these considerations lead to the description of complex (**1**) as a dioxo ylide complex (A) rather than an 'oxo-metallobetaine' (B).



(A) (B)

In spite of the considerable amount of work on the chemistry of phosphorus ylides with transition metal complexes,[4] compound (**1**) constitutes the first example of a dioxo-phosphorus ylide complex.

Besides the interest of complex (**1**) as a key intermediate in the formation of compound (**2**) it constitutes a rare example of a transition metal species bearing on the same metal oxo groups and organic ligands. Phosphorus ylide dioxo complexes such as (**1**) can be considered as a first step of an alkylation reaction of dioxo species and, therefore, comparable to a portion of surface oxides and could be used as a model for the understanding of heterogeneous catalytic processes.

The chemical properties of complex (**1**) which reacts at room temperature under a low pressure of CO are now being actively investigated.

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† Compound (**1**) crystallizes in the monoclinic space group $P2_1/n$ with a = 9.070(3), b = 14.728(5), c = 23.49(1) Å; β = 92.37(3)° and U = 3135(3) $Å^3$; D_C = 1.23 g cm^{-3}. M_r = 582.55, Z = 4. A crystal of dimensions 0.1 × 0.4 × 0.5 mm^3 was studied protected by silicone grease. Diffraction data were collected with a CAD 4 Enraf-Nonius diffractometer, Mo-K_α radiation (λ = 0.71073 Å), $\theta_{max.}$ = 23°. Intensities were not corrected for absorption (μ = 4.8 cm^{-1}). The structure was solved and refined with the SDP software (Frenz 1978) by a combination of Patterson, difference-Fourier and full-matrix least-squares refinement techniques using anisotropic thermal parameters for all non-hydrogen atoms. The final conventional residual was R = 0.049 and R_w = 0.061 for 2799 reflections and 520 variables. 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, 1986.

‡ The $^{31}P\{^1H\}$ n.m.r. spectrum in C_5D_5N shows one peak at 36.3 p.p.m.