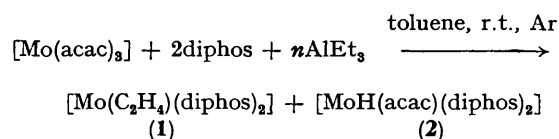


π -Ethylene Complex of Molybdenum(0) and Hydrido(acetylacetonato)-complex of Molybdenum(II) with Diphosphine Ligands

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Summary Treatment of [Mo(acac)₃] and diphos in toluene with AlEt₃ under argon yielded a new ethylene-co-ordinated complex, [Mo(C₂H₄)(diphos)₂], (1) together with a hydride complex, [MoH(acac)(diphos)₂], (2) whose characterization and reactions are described.



RECENTLY low-valent molybdenum compounds have been reported with special reference to their unique role in the olefin metathesis reaction and nitrogenase models. However, examples of isolated low-valent molybdenum complexes with no carbonyl ligands are limited, and a simple olefin-co-ordinated complex of molybdenum(0) has not been reported. We now describe the preparation, characterization, and some reactions of the title complexes.

It is known that the treatment of [Mo(acac)₃] (acac = acetylacetonate) with AlEt₃ in the presence of diphos (Ph₂PCH₂CH₂PPh₂) in toluene under dinitrogen at room temperature affords the bis-dinitrogen complex, *trans*-[Mo(N₂)₂(diphos)₂].¹ When the same reaction was carried out under argon in place of dinitrogen, orange prisms of [Mo(C₂H₄)(diphos)₂] (1) and brown needles of [MoH(acac)(diphos)₂] (2) were formed.

The ratio of the products (1) and (2) depended on the amount of AlEt₃ used; >5 mol. equiv. of AlEt₃ gave orange complex (1) (22%) almost exclusively, whereas use of 2—3 mol. equiv. of AlEt₃ gave brown needles of complex (2) (57%). Both (1) and (2) were obtained by the use of 3—5 mol. equiv. of AlEt₃.

The diamagnetic complex (1) is moderately stable in air, soluble in THF, hot toluene, and hot benzene, and can be recrystallized from these solvents. Its i.r. spectrum (KBr disc) showed a weak band at 2959 cm⁻¹ assignable to the co-ordinated ethylene. Thermolysis, iodolysis, alcoholysis, and hydrolysis of (1) evolved 73—109% of the theoretical amount of ethylene. The ¹H n.m.r. spectrum of (1) (CD₂Cl₂; 100 MHz; r.t.) showed co-ordinated ethylene protons at δ 2.16 (d), CH₂(diphos) at δ 2.8 br (s), and Ph protons at δ 6.6—7.4.

On passing dinitrogen gas into a refluxing solution of (1) in toluene, complex (1) is converted into the bis-dinitrogen complex, *trans*-[Mo(N₂)₂(diphos)₂], (3).¹⁻³ Conversely, the bis-dinitrogen complex was converted into the ethylene complex (1) by passing C₂H₄ through a boiling toluene solution of (3).

The reaction of (1) with tetracyanoethylene (TCNE) in toluene yielded a purple complex, [Mo(TCNE)₂(diphos)₂], accompanied by the evolution of C₂H₄. The reaction of (1) or (3) with carbon dioxide in toluene under reflux yielded *cis*-[Mo(CO)₂(diphos)₂]⁴ (49%) and diphosphine oxide.

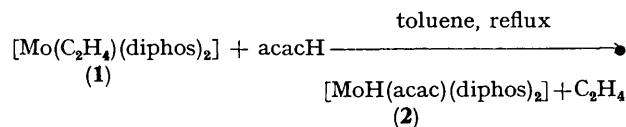
The diamagnetic brown complex (2) is soluble in THF, benzene, and toluene. The i.r. spectrum (KBr disc) of (2) showed a band at 1803 cm⁻¹ ascribable to ν(Mo-H) together with bands from co-ordinated acac [1560 s, ν(C=C); 1510 s, ν(C=O); 1390 s, δ(aCH₃); 1265 m, ν(C-C); and 766 w, π(C-H)] and diphos. The ¹H n.m.r. spectrum of (2) (C₆D₆; 100 MHz; r.t.) showed an Mo-H resonance at δ -4.1 (m) and CH₃ and CH (acac) resonances at δ 1.16 (s) and 4.14 (s), respectively, together with diphos resonances.

From the reaction mixture of (2) and D₂SO₄, deuteriated acetylacetone was extracted by Et₂O in 60% yield determined spectrophotometrically. The isolation of analytically pure [MoH(acac)(diphos)₂] was impossible owing to the

difficulty of separating diphos from the complex [*M* (cryoscopically in benzene), 600 ± 100. Calc. for C₅₇H₅₆O₃P₄Mo; 993].

Alkyl complexes containing both acac and tertiary phosphine ligands are known for nickel,⁵ cobalt,⁶ iron,⁷ and platinum,⁸ but analogous hydride complexes are not known.

Treatment of (1) with acetylacetone in refluxing toluene afforded complex (2), releasing C₂H₄.



When 3,3-dideuteriopentane-2,4-dione was used in place of acacH, [MoD([²H₁]acac)(diphos)₂] was obtained. The ν(Mo-H) band at 1803 cm⁻¹ partially shifted to 1295 cm⁻¹ on deuteration. A similar reaction was also observed with *trans*-[Mo(N₂)₂(diphos)₂] (3). These reactions, which support the structure assigned to (2), represent the first reported example of oxidative addition of acacH.

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