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 AlEt$_3$ under argon yielded a new ethylene-co-ordinated complex, [Mo(C$_2$H$_4$)(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 AlEt$_3$ in the presence of diphos (Ph$_2$PCH$_2$CH$_2$PPh$_2$) in toluene under dinitrogen at room temperature affords the bis-dinitrogen complex, *trans*-[Mo(N$_2$)$_2$(diphos)$_2$].[1] When the same reaction was carried out under argon in place of dinitrogen, orange prisms of [Mo(C$_2$H$_4$)(diphos)$_2$] (**1**) and brown needles of [MoH(acac)(diphos)$_2$] (**2**) were formed.

$$[\mathrm{Mo(acac)_3}] + 2\mathrm{diphos} + n\mathrm{AlEt_3} \xrightarrow{\text{toluene, r.t., Ar}} \underset{(\mathbf{1})}{[\mathrm{Mo(C_2H_4)(diphos)_2}]} + \underset{(\mathbf{2})}{[\mathrm{MoH(acac)(diphos)_2}]}$$

The ratio of the products (**1**) and (**2**) depended on the amount of AlEt$_3$ used; >5 mol. equiv. of AlEt$_3$ gave orange complex (**1**) (22%) almost exclusively, whereas use of 2—3 mol. equiv. of AlEt$_3$ gave brown needles of complex (**2**) (57%). Both (**1**) and (**2**) were obtained by the use of 3—5 mol. equiv. of AlEt$_3$.

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 ^{1}H n.m.r. spectrum of (**1**) (CD$_2$Cl$_2$; 100 MHz; r.t.) showed co-ordinated ethylene protons at δ 2·16 (d), CH$_2$(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$(N_2)_2$(diphos)$_2$], (**3**).[1–3] Conversely, the bis-dinitrogen complex was converted into the ethylene complex (**1**) by passing C_2H_4 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 C_2H_4. 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 m 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(aCH$_3$); 1265 m, ν(C–C); and 766 w, π(C–H)] and diphos. The ^{1}H n.m.r. spectrum of (**2**) (C_6D_6; 100 MHz; r.t.) showed an Mo–H resonance at δ −4·1 (m) and CH_3 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 D_2SO_4, deuteriated acetylacetone was extracted by Et_2O 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 $C_{57}H_{56}O_2P_4Mo$; 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 C_2H_4.

$$\underset{(\mathbf{1})}{[\mathrm{Mo(C_2H_4)(diphos)_2}]} + \mathrm{acacH} \xrightarrow{\text{toluene, reflux}} \underset{(\mathbf{2})}{[\mathrm{MoH(acac)(diphos)_2}]} + \mathrm{C_2H_4}$$

When 3,3-dideuteriopentane-2,4-dione was used in place of acacH, [MoD([$^2H_1$]acac)(diphos)$_2$] was obtained. The ν(Mo–H) band at 1803 cm^{-1} partially shifted to 1295 cm^{-1} on deuteriation. A similar reaction was also observed with *trans*-[Mo$(N_2)_2$(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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