

Preliminary communication

DINITROGEN VERSUS η^6 -ARENE COORDINATION IN METHYLDIPHENYLPHOSPHINE COMPLEXES OF MOLYBDENUM(0)

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Summary

High yield syntheses and properties of the new complexes $\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{-PMePh})(\text{PMePh}_2)_2$ (**1**), $\text{L} = \text{PMePh}_2$ and $\text{P}(\text{OMe})_3$, are reported along with new direct preparations of $\text{Mo}(\text{N}_2)_2(\text{PMePh}_2)_4$ and $\text{Mo}(\eta^6\text{-C}_6\text{H}_6)(\text{PMePh}_2)_3$.

High yields (70–80%) of crystalline *trans*- $\text{Mo}(\text{N}_2)_2(\text{PMePh}_2)_4$ (**1**) and the new complex $\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{PMePh})(\text{PMePh}_2)_3$ (**2**) are simply obtained by reducing $\text{Mo}_2\text{Cl}_{10}$ and PMePh_2 (8 mol) with excess magnesium in rigorously dry THF under N_2 or Ar, respectively. The dinitrogen complex readily rearranges and coordinates η^6 -arene ligands. Thus these reactions provide convenient entries into η^6 -arene-molybdenum chemistry accessible before only by metal vapour synthesis [1] or difficult reduction procedures [2].

The direct reduction and work-up procedures reported by George and Noble [3] were followed to prepare **1** except that magnesium was used and found to be a cleaner, faster reductant (30 minutes at 25°C) than Na/Hg amalgam. When preparing the dinitrogen complex, the solution must be well saturated with N_2 to avoid gas diffusion problems which result in the contamination of **1** by **2**. Due to their similar orange colours, solubilities and infrared spectra (apart from $\nu(\text{N}_2)$ 1925 cm^{-1} for **1**), compound **2** has not been recognized in the past as an impurity in **1**, and this has complicated the assignment of ^{31}P NMR spectra of **1** [4]. The pure dinitrogen complex gives a singlet in C_6H_6 at 18.1 ppm (not 38 ppm [4]) relative to 85% H_3PO_4 whereas **2** gives singlets at 33.2 ppm (three nuclei, equivalent because of ring rotation) and –32.0 ppm (the dangling phosphorus atom whose chemical shift is near uncoordinated ligand at –28.6 ppm).

In a typical preparation of **2**, $\text{Mo}_2\text{Cl}_{10}$ (1.3 g) was dissolved in a solution of PMePh_2 (4.8 g) in THF (50 ml) under Ar or in vacuo. Activated Grignard

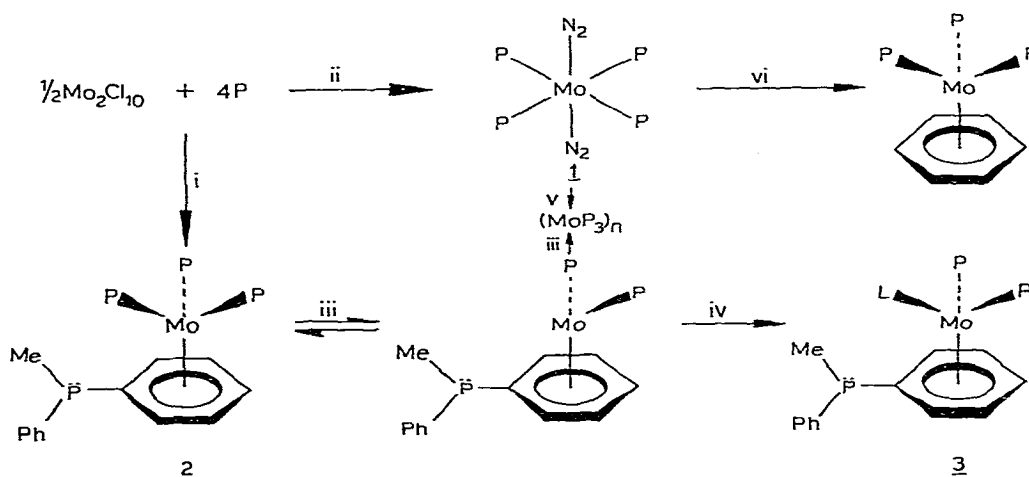
magnesium (2.1 g) was then added and the mixture was stirred for 45 min. Filtration and evaporation of the THF gave a brown residue which was extracted with benzene (30 ml). This solution was filtered through celite, concentrated in vacuo and treated with methanol (15 ml) to yield **2** as an air sensitive orange powder (3.1 g, 75%).

A similar compound, $\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{PMe}_2)(\text{PMe}_2\text{Ph})_3$, has been prepared in very poor yield by a different method [5] but only its crystallographic features have been reported [6]. Recently $\text{Mo}(\eta^6\text{-4-CH}_3\text{OC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_4\text{OCH}_3\text{-4})_2)$ (triphos) has been synthesized and characterized by ^{31}P NMR [7].

The chiral nature of the η^6 -bonded phosphine ligand in **2** is clearly indicated in the ^1H NMR spectrum (200 MHz, C_6D_6) where distinct resonances at δ 3.57 and 3.71 ppm are observed for the diastereotopic protons *ortho* to the phosphorus on the η^6 -arene: δ 1.20 (d, J 4.8 Hz, 3, CH_3 on dangling P), 1.77 (broad, 9, P-CH_3), 3.57 (m, 1, *ortho*-C-H), 3.71 (m, 1, *ortho*-C-H), 4.14 (m, 2, meta C-H), 4.40 (m, 1, *para*-C-H), and 7.0–7.5 (m, 35, C_6H_5) ppm.

Apparent in the ^1H but not in the ^{31}P NMR spectra of **2** are small resonances due to as yet uncharacterized oligomers, $\{\text{Mo}(\text{PMePh}_2)_3\}_n$, at δ 1.48 (d, J 4.9 Hz), 1.61 (d, J 4.3 Hz), 1.62 (d, J 3.9 Hz), 3.02 (m), 3.92 (m) ppm and free phosphine at δ 1.37 ppm (d, J 3.9 Hz) that grow in with time as a labile σ -bonded ligand dissociates from **2**. Complex **2** must be recrystallized (benzene/MeOH) in the presence of excess ligand to minimize the formation of these oligomers. However it has not yet been prepared totally free of oligomers and analyzes for approximately $\text{Mo}(\text{PC}_{13}\text{H}_{13})_{3.8}$. Found: C, 69.20; H, 6.01. Calcd.: C, 69.26; H, 5.81%.

A labile phosphine of **2** is readily substituted by the small ligand $\text{P}(\text{OMe})_3$ as in Scheme 1 to give the monosubstituted product $\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{PMePh})(\text{PMePh}_2)_2(\text{P}(\text{OMe})_3)$ (**3**), which was isolated as an air sensitive orange solid (80% yield) by adding methanol. The ^{31}P NMR spectrum of **3** in C_6H_6 shows



SCHEME 1. $\text{P} = \text{PMePh}_2$; (i) excess Mg, THF, Ar, 25°C ; (ii) excess Mg, THF, N_2 , 25°C ; (iii) dissociation of P and oligomerization; (iv) $\text{L} = \text{P}(\text{OMe})_3$ (1 mol), THF, 25°C ; (v) THF, Ar, 67°C ; (vi) benzene, Ar, 80°C .

the phosphite phosphorus resonance at 175.72 ppm as a multiplet due to coupling to two diastereotopic phosphine ligands at 38.61 ppm (J 52.49 Hz) and 37.91 ppm (J 53.71 Hz) as well as to the dangling phosphorus at -28.72 ppm (J 2.44 Hz). Coupling between the phosphine ligands was too small to be resolved. Proton NMR (60 MHz, C_6D_6) data for **3**: δ 1.42 (d, J 4 Hz, CH_3 on dangling P), 1.84 (d, J 5 Hz, 3, P- CH_3), 1.92 (d, J 5 Hz, 3, P- CH_3), 3.30 (d, J 10 Hz, 9, P(OCH_3)₃), 3.57 (m, 1, *ortho*-C-H), 3.69 (m, 1, *ortho*-C-H), 4.4 (m, 3, *meta+para*-C-H), 7.0-8.0 (m, 25, P- C_6H_5). Again diastereotopic arene and methyl proton resonances are observed. Elemental analyses for **3** recrystallized from THF/MeOH: Found: C, 61.34; H, 5.76. $C_{42}H_{48}MoO_3P_4$ calcd.: C, 61.47; H, 5.90%.

We have as yet not been able to convert **1** into **2** by heating or UV irradiation under Ar; instead oligomers $\{Mo(PPh_2Me)_3\}_n$ form. The latter are the main products from the irradiation of $MoH_4(PMePh_2)_4$ under N_2 , along with free $PMePh_2$ and traces of the dinitrogen complex **1** that was thought to form cleanly under these conditions [8].

Complex **1** reacts with arene solvents. For example, when heated under Ar in benzene, complex **1** rearranges to the known complex $Mo(\eta^6-C_6H_6)-(PMePh_2)_3$ [9] which is isolated in 40% yield (see Scheme 1). We have found that these η^6 -arene complexes have a rich chemistry because of the lability of the phosphine ligands [10].

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