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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 Mo(η^6-C_6H_5-PMePh)($PMePh_2$)$_2$(L), L = $PMePh_2$ and $P(OMe)_3$, are reported along with new direct preparations of Mo(N_2)$_2$($PMePh_2$)$_4$ and Mo(η^6-C_6H_6)($PMePh_2$)$_3$.

High yields (70–80%) of crystalline *trans*-Mo(N_2)$_2$($PMePh_2$)$_4$ (1) and the new complex Mo(η^6-C_6H_5PMePh)($PMePh_2$)$_3$ (2) are simply obtained by reducing Mo_2Cl_{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 $\nu(N_2)$ 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, Mo_2Cl_{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

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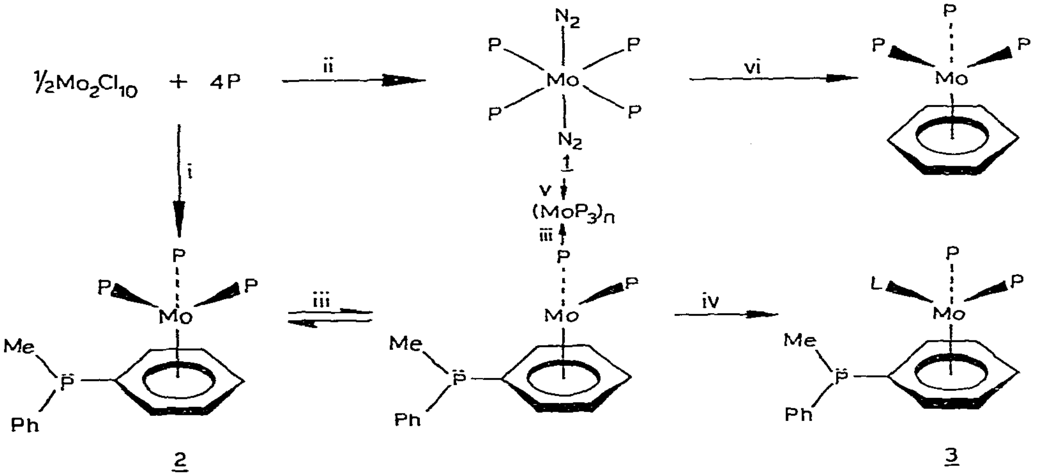
magnesium (2.1 g) was then added and the mixture was stirred for 45 min. Filtration and evaporation of the THF gave a brown residue which was extracted with benzene (30 ml). This solution was filtered through celite, concentrated in vacuo and treated with methanol (15 ml) to yield **2** as an air sensitive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

A similar compound, $Mo(\eta^6\text{-}C_6H_5PMe_2)(PMe_2Ph)_3$, has been prepared in very poor yield by a different method [5] but only its crystallographic features have been reported [6]. Recently $Mo(\eta^6\text{-}4\text{-}CH_3OC_6H_4P(C_6H_4OCH_3\text{-}4)_2)$(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, $\{Mo(PMePh_2)_3\}_n$, 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 $Mo(PC_{13}H_{13})_{3.8}$. 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 $P(OMe)_3$ as in Scheme 1 to give the monosubstituted product $Mo(\eta^6\text{-}C_6H_5PMePh)(PMePh_2)_2(P(OMe)_3)$ (**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. P = $PMePh_2$; (i) excess Mg, THF, Ar, 25°C; (ii) excess Mg, THF, N_2, 25°C; (iii) dissociation of P and oligomerization; (iv) L = $P(OMe)_3$ (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 $Mo(\eta^6\text{-}C_6H_6)(PMePh_2)_3$ [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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