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Preliminary communication

Reaction of dihydrogen with bisdinitrogen complexes of molybdenum containing bidentate tertiary phosphine ligands

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Hidai[1] *et al.* reported that the reaction of $Mo(N_2)_2(Dppe)_2$ [Dppe = 1,2-bis(diphenylphosphino)ethane] with dihydrogen in benzene solution for three days gave *trans*-$MoH_2(Dppe)_2$ (I) but in toluene solution produced [*trans*-MoH_2(Dppe)]$_2$-μ-(Dppe) (II). I was converted into II in toluene solution while II was converted into I in benzene. It was stated that these compounds were insufficiently soluble in organic solvents to allow their molecular structure to be determined by NMR spectroscopy.

We wish to report the reaction of $Mo(N_2)_2(Dmpte)_2$ [2] (III) [Dmpte = 1,2-bis(di-*m*-tolylphosphino)ethane] with dihydrogen. The ligand Dmtpe* imparts excellent solubility properties to complexes that contain this ligand. When dihydrogen was bubbled through a cyclohexane solution of III for 4 h $MoH_4(Dmtpe)_2$ (IV) was formed almost quantitatively. The extent of reaction was monitored by the loss of $\nu(N{\equiv}N)$ in the IR spectrum and the appearance of hydride protons in the ^1H NMR spectrum.

IV can also be synthesized by the reduction of $MoCl_2(Dmtpe)_2$ [2] with 1% Na/Hg in THF under an atmosphere of dihydrogen. The yield of pure product was 82%: IR(CsI); ν(Mo–H) 1750 (m) cm^{-1}; δ(Mo–H) 761 (w) cm^{-1}.

The presence of four hydride hydrogen atoms per molecule was established from the ^{31}P and ^1H NMR spectral data that were recorded on a Varian XL-100 NMR spectrometer with the assistance of a Varian 620-I computer. All spectra were time-averaged. The room temperature 100.1 MHz hydride NMR spectrum of IV in C_6D_6 exhibits a 1/4/6/4/1 quintet centered at τ 13.6 (J(PH) 30 Hz). The ^1H NMR spectrum was also run in toluene and CH_2Cl_2 and shows the same quintet. At −70° in toluene the spectrum remains an apparent quintet, although the lines were significantly broader than at room temperature. Similar results are observed in CH_2Cl_2 down to −50°. The room temperature 40.5 MHz ^{31}P NMR spectrum of IV with selective decoupling of the phosphorus ligand protons in C_6D_6 shows

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* Dmtpe was prepared by the method used to synthesize Dppe[3].

a 1/4/6/4/1 quintet at −84 ppm (relative to 85% H_3PO_4). Meakin[4] *et al.* reported similar results for $MoH_4(Dppe)_2$ that was originally prepared[5] by the reduction of $MoCl_4(Dppe)$ with ethanolic $NaBH_4$ in the presence of an excess of Dppe.

This work suggests that the reaction of $Mo(N_2)_2L_2$ (L = Dppe, Dmtpe) with dihydrogen produces the tetrahydride MoH_4L_2, rather than the dihydrides reported by Hidai[1]. The ^1H NMR spectra run in C_6D_6 and toluene show no evidence of either MoH_2L_2 or [*trans*-$MoH_2L]_2$-μ-L. However, these results do not imply that compounds I and II do not exist.

Dinitrogen reacts with IV in cyclohexane solution to give $Mo(N_2)_2(Dmtpe)_2$; $\nu(N{\equiv}N)$ 2017 (vw) and 1960 (vs) cm^{-1} in CsI. The reaction is > 90% complete after 40 h.

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