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Preliminary communication

REACTIONS OF COORDINATED LIGANDS

V*. SYNTHESIS OF μ-(TETRAPHENYL DIPHOSPHINE)DECACARBONYLDIMOLYBDENUM

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Summary

By treatment of $(CO)_5MoPPh_2Cl$ with ethylmagnesium bromide $(CO)_5MoPPh_2PPh_2Mo(CO)_5$ has been obtained as an unanticipated product. The compound has been characterized by its physical and spectral properties.

Mono- and di-nuclear coordination complexes of tetraorganobipnictogens can be prepared by different procedures [1-10]. However, previous attempts to prepare $(CO)_5MPPh_2PPh_2M(CO)_5$, where M = Cr, Mo or W, have not been successful owing to the apparent thermal instability of these substances. We wish to report that $(CO)_5MoPPh_2PPh_2Mo(CO)_5$ has been obtained by us as an unanticipated product of the reaction between $(CO)_5MoPPh_2Cl$ and ethylmagnesium bromide.

The basic procedure involved the addition of 10 mmol of $(CO)_5MoPPh_2Cl$ in 15 ml of dry THF to 10 mmol of the Grignard reagent in 25 ml THF at 5°C under a nitrogen atmosphere. The mixture was hydrolyzed after one hour with 100 ml cold water and ether soluble materials were extracted. Evaporation of the ether extract yielded an oil which upon treatment with 10 ml of hexane yielded a solid precipitate. (A 17% yield of purified $(CO)_5MoPPh_2Et$ was subsequently obtained from the hexane soluble portion of the oil.) The solid material was recrystallized from an ether/ethanol mixture to give a 12% yield of a lemon-yellow, crystalline product, m.p. 168—169°C (dec.). The elemental analysis (Found: C, 48.15; H, 2.51. $C_{34}H_{20}Mo_2O_{10}P_2$ calcd.: C, 48.45; H, 2.38%), molecular weight of ~870 (cryoscopic benzene), and metal carbonyl stretching bands at 2072m, 1984w, 1925s and 1945s cm^{-1} (characteristic of a $(CO)_5MoL$ complex [11]) suggest that the complex is $(CO)_5MoPPh_2PPh_2$-$Mo(CO)_5$. Although the mass spectrum of this compound does not reveal the

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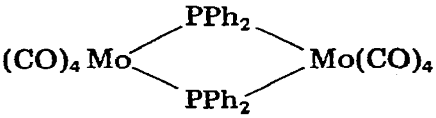
*For part IV see ref. 15.

expected parent peak at m/e 846 (^{98}Mo), significant lines in the higher mass region are found at m/e values of 580 (^{98}Mo), 524 (^{98}Mo) and 468 (^{98}Mo) which correspond to $Mo(CO)_nPPh_2PPh_2$ with $n = 4$, 2 and 0, respectively. While it is possible that each of these ions could be an ion of the general form $Mo(CO)_n(PPh_2)_2$, we note that the presence of a strong line (one of the strongest in fact) at m/e 370 is best accounted for by the presence of Ph_2PPPh_2 as a ligand. Further evidence that the isolated compound is in fact $(CO)_5MoPPh_2PPh_2Mo(CO)_5$ is provided by the observation that upon heating the compound to 170°C gas is evolved, color changes occur and a deeply colored solid is produced which can be recrystallized from methyl ethyl ketone as an orange solid, m.p. 290—300°C (dec.). This melting point, the color and infrared bands for the compound found at 2027s and 1961vs cm^{-1} ($CHCl_3$), which are as expected for a *cis*-disubstituted complex [11], all agree favorably with the properties reported for  $(CO)_4Mo\begin{smallmatrix}PPh_2\\ \\ PPh_2\end{smallmatrix}Mo(CO)_4$ by Chatt and Thornton [9]. These investigators obtained this di-bridged phosphido complex by heating tetraphenylbiphosphine and $Mo(CO)_6$ at 190°C for 30 hours. Obviously, at this temperature, any $(CO)_5MoPh_2PPPh_2$-$Mo(CO)_5$ formed in a direct reaction would not survive as we have shown here.

Additional preliminary studies have shown that $Mo(CO)_5PPh_2Cl$ will react with magnesium metal in THF, slowly at room temperature and more rapidly under reflux, to produce both $(CO)_5MoPPh_2PPh_2Mo(CO)_5$ and $(CO)_4Mo(PPh_2)_2$ Douglas and Ruff [12] have indicated that mercury and other unspecified metals did not lead to coupling of the ligands in $(CO)_4FePF_2Br$. In another reaction, we have noted that $(CO)_5MoPMe_2PMe_2$-$Mo(CO)_5$ is formed in very low yield in the reaction of $(CO)_5MoPMe_2Cl$ with methylmagnesium iodide; $(CO)_5MoPMe_3$ was the major product isolated. Both materials were identified positively by comparison of their physical and spectral properties to reported values [8,13].

This new coupling reaction is formally analogous to the well-known anomalous reaction of Grignard reagents with halophosphine sulfides [14]. Other reactions of various organometallic reagents with coordinated halophosphine ligands will be reported at a later time.

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