Bis-adducts of Group VIII Metal Bisdithiobenzil Complexes with Phosphines

By V. P. MAYWEG and G. N. SCHRAUZER*
(*Shell Development Company, Emeryville, California*)

IN a recent communication it was reported that several compounds described by us as bisphosphine adducts of Group VIII metal bisdithiodiketone complexes,[1] $MS_4C_4R_4{\cdot}2PR'_3$, are actually substitution products of composition $MS_2C_2R_2{\cdot}2PR'_3$,[2] (I). We have re-investigated these compounds which we had previously described only briefly and now find that they are indeed of composition (I). However, in this Communication we report that bisphosphine adducts of Group VIII metal bisdithiobenzil complexes are nevertheless capable of existence and isolable. Both $NiS_4C_4Ph_4$ and $PdS_4C_4Ph_4$ react with tetraphenylethylenediphosphine in benzene at room temperature to produce complexes of composition $MS_2C_2Ph_2{\cdot}Ph_2PCH_2{\cdot}CH_2PPh_2$ plus a mixture of 2-phenylthionaphthene and tetraphenylthiophen. The latter are condensation products of the dithiobenzil released during the reaction.[3] The platinum compound, $PtS_4C_4Ph_4$, under similar conditions afforded a blue, diamagnetic, crystalline *adduct* $PtS_4C_4Ph_4{\cdot}Ph_2PCH_2{\cdot}CH_2PPh_2$ (II). Complex (II) is stable in the solid state and readily soluble in nonpolar solvents, forming light-sensitive solutions. On irradiation it decomposed into $PtS_2C_2Ph_2{\cdot}Ph_2PCH_2{\cdot}CH_2PPh_2$ and the condensation products of dithiobenzil. On heating above the decomposition point of 186° it decomposed in a similar fashion, but 20% of the products consisted of $PtS_4C_4Ph_4$ and the phosphine. Reaction of $PtS_4C_4Ph_4$ with tributylphosphine in benzene at room temperature also afforded a diamagnetic bis-adduct, $PtS_4C_4Ph_4{\cdot}2PBu^n_3$ (III). Crystals of (III) decomposed at 162° into the starting materials, and solutions of (III) were essentially unaffected by light. Bisdithiobenzilnickel, on standing, slowly reacted with tributylphosphine as well as triphenylphosphine in benzene solution at room temperature, affording brown, crystalline adducts $NiS_4C_4Ph_4{\cdot}2PR_3$. These are much less stable than those of the platinum complex. On heating to about 120° quantitative decomposition into the starting components was observed. In solution, the original brown colour changes slowly to green on heating; the adducts may be recrystallized, however, from a mixture of CH_2Cl_2/n-hexane in the presence of an excess of the phosphine. The adducts appear to form only in the cold. It is possible, in fact, to heat $NiS_4C_4Ph_4$ in molten triphenylphosphine up to about 230° without disappearance of the characteristic green colour of the complex. On cooling, a mixture of crystalline $NiS_4C_4Ph_4$ and triphenylphosphine is recovered. Above 230° the nickel complex decomposed largely into nickelous sulphide and 2-phenylthionaphthene. A solution of $NiS_4C_4Ph_4$ in liquid tributylphosphine remained green up to 230°, but in the cold the formation of the bis-adduct was observed to take place over a period of several hours. Attempts to isolate similar adducts of $PdS_4C_4Ph_4$ were unsuccessful. This complex underwent the substitution reaction instead; addition of tributylphosphine to a suspension of the complex in benzene yielded a brown oil which was rapidly converted into the red crystals of $PdS_2C_2Ph_2{\cdot}2PR_3$. The latter complex was also prepared with triphenylphosphine and was found to cleave off one molecule of phosphine reversibly on heating the solution. A dimeric $Pd_2S_4C_4Ph_4{\cdot}2PPh_3$ (IV)

* Present address: Department of Chemistry, University of California at San Diego, La Jolla, California.

(green crystals, dec. p. 282°) was isolated from this reaction mixture. On prolonged heating of solutions of (IV), decomposition into the insoluble $(PdS_2C_2Ph_2)_x$ took place.[4] In the infrared spectra of all adducts isolated, the characteristic bands of the metal bisdithione system are absent. Similarly, in the electronic spectra the intense band around 800 mμ was missing, indicating that the ligands are no longer present in their original delocalized state. Although it is probable that the phosphines are co-ordinated to the metals, it must be pointed out that they could also interact with the sulphur atoms of the ligands. *X*-Ray-structural determinations are necessary to decide on this issue.

(*Received, August* 12*th*, 1966; *Com.* 593.)

[1] G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, 1965, **87**, 1483.

[2] A. Davison and D. V. Howe, *Chem. Comm.*, 1965, 200. Our previous structural assignment was caused by numerical coincidences in the analyses.

[3] Elemental sulphur is formed during this reaction and reacts with the phosphine. Accordingly, the respective phosphine sulphides could also be isolated from the reaction mixture.

[4] Satisfactory analyses were obtained for all complexes described.