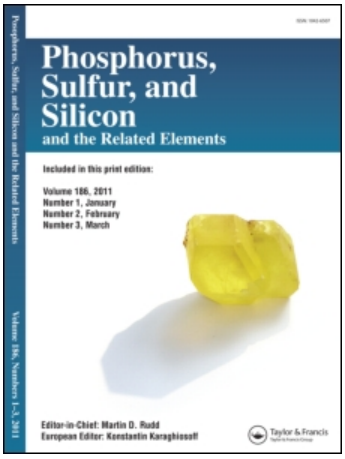

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Bis(diphenylphosphino)Alkane / Co(II)/Tetrahydroborate and Cyanotrihydroborate Reactions: Formation of Unusual Bis(diphenylphosphino)methane Complexes and the Influence of Carbon Monoxide

D. J. Elliot[a]; D. G. Holah[a]; A. N. Hughes[a]; S. Maciaszek[a]; J. D. Thompson[a]; V. R. Magnuson[b]; K. O. Parker[b]
[a] Department of Chemistry, Lakehead University, Ontario, Canada [b] Department of Chemistry, University of Minnesota-Duluth, Duluth, Minnesota, U.S.A.

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Bis(diphenylphosphino)Alkane / Co(II) / Tetrahydroborate and Cyanotrihydroborate Reactions: Formation of Unusual Bis(diphenylphosphino)methane Complexes and the Influence of Carbon Monoxide

D.J. Elliot, D.G. Holah, A.N. Hughes*, S. Maciaszek, and J.D. Thompson, Department of Chemistry, Lakehead University, Thunder Bay, Ontario, Canada. P7B 5E1

and

V.R. Magnuson and K.O. Parker, Department of Chemistry, University of Minnesota-Duluth, Duluth, Minnesota 55812, U.S.A.

Reactions between Co(II), bis(diphenylphosphino)methane (dppm) and either $NaBH_4$ or $NaBH_3CN$ have been studied. They follow pathways which are in marked contrast to those followed by $Ph_2P(CH_2)_nPPh_2$ (n = 2-6) in the presence of $NaBH_4$ in which the final product is normally $CoH(phosphine)_2$ although binuclear BH_4-bridged complexes may sometimes be obtained. The products obtained with dppm are $Co_2X_3(dppm)_2$ (X=Cl,Br) (I), $CoCl(dppm)_3$ (II), $\{CoHX(dppm)_2\}Y$ (X=Cl,Br,I,BH_3CN; Y=Cl,BH_3CN,BPh_4,ClO_4) (III), and $Co_2H_2(dppm)_3$ (IV). While a binuclear A-frame structure can be proposed for the Co(I)-Co(II) species (I), crystal twinning has so far prevented an X-ray determination. However, X-ray studies on (II) and (IV) have shown that (II) contains tetrahedral Co(I) to which one chloro and three monodentate dppm ligands are attached while (IV) is a binuclear species containing bridging dppm ligands and two terminal hydrides. The compounds (III) are octahedral Co(III) complexes. Possible mechanisms for the formation of these in strongly reducing environments will be discussed.

Some of these reactions have also been carried out under CO and similarities of behaviour of dppm and diphos (n=2) then appear. Thus, $\{Co(CO)(phosphine)_2\}X$ (X=BH_3CN,BPh_4) have been obtained for both phosphines and these reactions also produce Co(III)-diphos complexes related to (III). New Co-CO-phosphine clusters containing multiple terminal and bridging CO groups have also been produced.