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Preliminary communication

BASE INDUCED ADDITIONS OF COORDINATED PHOSPHINES TO ACETYLENES TO GIVE METAL COMPLEXES OF CHELATING DIPHOSPHINE LIGANDS

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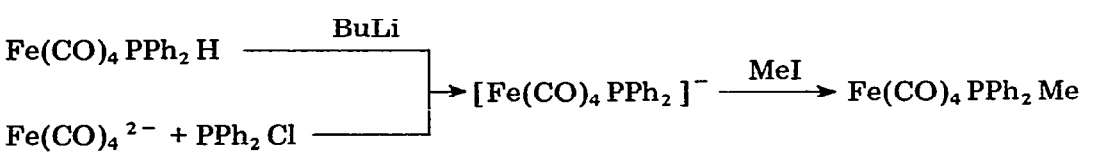
Summary

Reactions occur with $[M(CO)_4(PPh_2H)(PPh_2)]^-$ (M = Cr, Mo) and $[Mn(CO)_3(PPh_2H)(PPh_2)Br]^-$ (each generated from the corresponding bisphosphine metal carbonyl and BuLi at —78°C) and several acetylenes with electron-withdrawing substituents (MeOOCC≡CCOOMe, PhC≡CCOOEt, PhC≡CH) to give after protonation, moderate yields of complexes of chelating diphosphines. These reactions are believed to be a type of Michael addition, proceeding via carbanion intermediates. Several isomers are possible in these reactions depending on the orientation of the acetylene substituent groups. *Trans*-stereochemistry of the single product derived from the manganese complex and MeOOCC≡CCOOMe was determined from NMR data; this preference is likely a consequence of steric constraints.

Complexes of secondary phosphines, when treated with bases of sufficient strength, give up a proton forming phosphidometal complexes. These phosphido complexes, in turn, are basic and may enter into reactions involving the nucleophilic phosphorus center such as the displacement of halide from alkyl halides [1,2]. Illustrative of this chemistry is the reaction sequence:

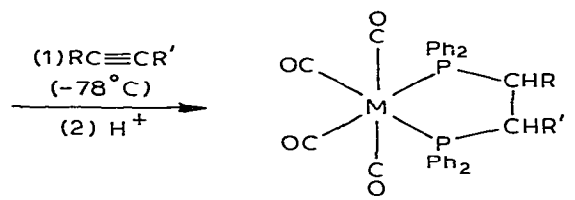


An alternative route to the phosphide intermediate is noted [3].

Extending this work, we report several reactions of *cis*-diphosphinemetal complexes with certain acetylenes in the presence of an equimolar (1/1)

amount of base, which yield after protonation new metal complexes of chelating diphosphines. Preliminary results are summarized in the equations below; data on the products are given in Table 1.

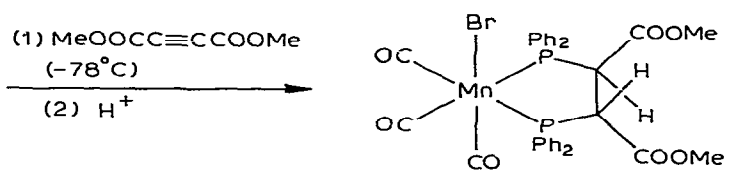
$$cis\text{-}M(CO)_4(PPh_2H)_2 \xrightarrow[-78\,^\circ C]{BuLi,\ THF} cis\text{-}[M(CO)_4(PPh_2H)(PPh_2)]^-$$



(I, M = Cr;
II, M = Mo)

(M = Cr, Mo; a, RC≡CR' = MeOOCC≡CCOOMe; b, RC≡CR' = PhC≡CCOOEt;
c, RC≡CR' = PhC≡CH)

$$fac\text{-}Mn(CO)_3(PPh_2H)_2Br \xrightarrow[-78\,^\circ C]{BuLi,\ THF} fac\text{-}[Mn(CO)_3(PPh_2H)(PPh_2)Br]^-$$



(III)

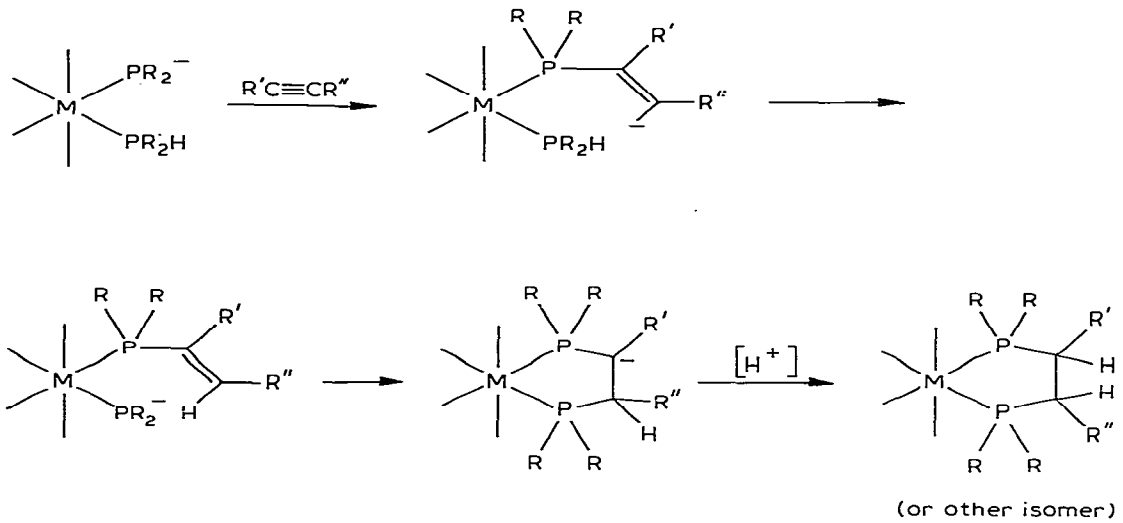
TABLE 1

PRODUCTS OF CYCLIZATION REACTIONS

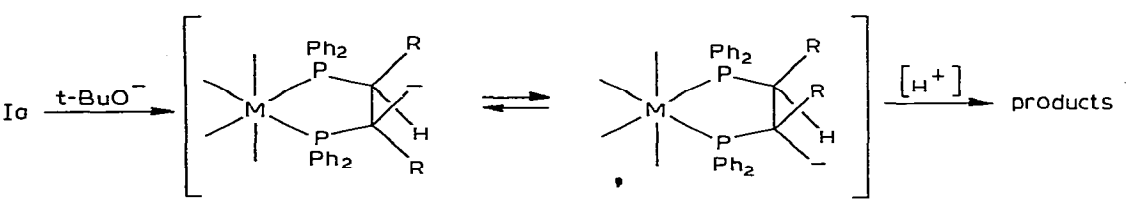
	Product data	Yield (%)
Ia	Isomer 1, green crystals, m.p. 203—204°C	25
	Isomer 2, green crystals, m.p. 218—219°C	31
Ib	Green crystals, m.p. 214—215°C	64
Ic	Green crystals, m.p. 203—205°C	23
IIa	Isomer 1, white crystals, m.p. 214—215°C	22
	Isomer 2, pale yellow crystals, dec. 223°C	35
IIb	White crystals, m.p. 197—198°C	27
IIc	White crystals, dec. 180°C	56
III	Orange crystals, dec. 191°C	18

The mild conditions required to effect this reaction are striking. Deprotonation of the phosphine by BuLi occurs at −78°C [1,2]. Addition of the acetylene at this temperature is followed by rapid color change over a few minutes. The reaction mixture is then allowed to warm to room temperature, and quenched with a proton donor. Product yields were low to moderate (18—64%) in the examples cited. The reactions were unsuccessful using dialkyl acetylenes.

The mechanism by which these reactions occur is believed to be a variant of the Michael reaction. Nucleophilic attack by the coordinated phosphide on the acetylene initially gives a carbanion. This abstracts a proton from the neighboring phosphine and the sequence then repeats itself. Protonation on workup gives the resulting product. A requisite for the reaction is the stabilization of the intermediate carbanions by the substituent group R or R′; this explains why the reaction is found to occur only with acetylenes with electron-withdrawing substituents.



In the reaction of the chromium and molybdenum complexes with MeOOCC≡CCOOMe the product occurs in two separable isomeric forms, differing in the orientations of the COOMe groups, *cis* or *trans* on the five-membered chelating ring. The relative amounts of these two isomers depends on the acid strength of the protonic reagent used in the workup. In a separate experiment the product mixture Ia in THF (ratio of isomers 1.2/1.0) was deprotonated with t-butoxide ion (25°C, 2 h) and then reprotonated. Using HCl (aq) the ratio of isomers is 1.2/1.0, with isobutyric acid (pK_a 4.84) the ratio increases to 3.8/1.0, and with water (pK_a 16) it is 9/1. Presumably the carbanionic intermediate is pyramidal and able to invert rapidly:



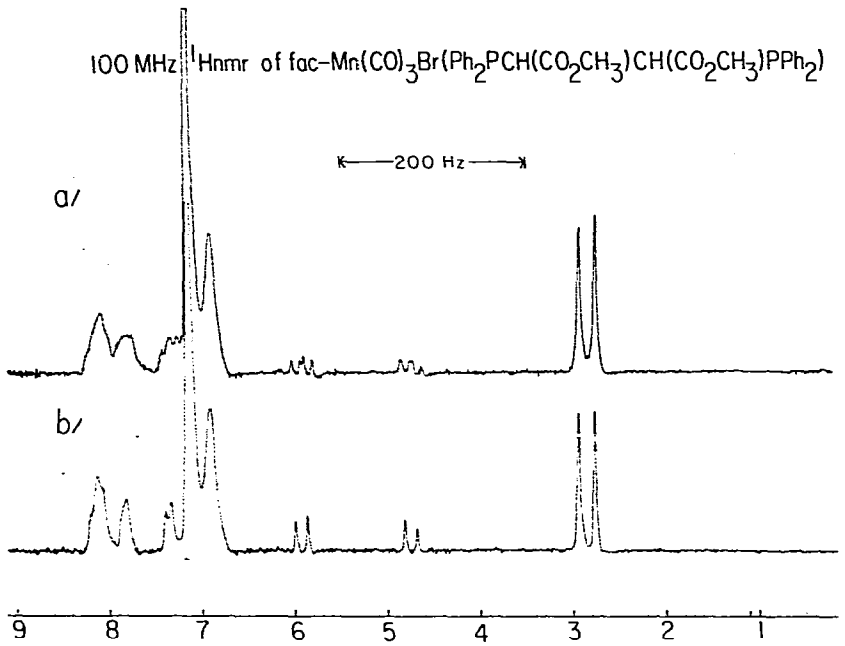


Fig.1. a/ ^{31}P coupled spectrum in C_6D_6 b/ ^{31}P decoupled spectrum

Rapid protonation (HCl) freezes the equilibrium, trapping the less stable configuration, whereas slower protonation by substances like water gives the more stable product by allowing the equilibrium to adjust as the reaction proceeds.

The reaction of the manganese complex with this acetylene gave only a single product whose stereochemistry, having *trans*-COOMe groups, could be unequivocally determined by proton NMR. The AB pattern associated with the methylene hydrogens in the $^1H\{^{31}P\}$ spectrum (Fig. 1) could only result from the *trans*-configuration in which these protons are in dissimilar environment. This is the product predicted on steric grounds; we may infer that the more stable isomers in the Cr and Mo reactions also have a *trans*-configuration.

We note in passing that complementary work in this area has also been reported. Johnson and Carty [4] report additions of secondary phosphines to the triple bond in alkynylphosphine complexes having the formula $M(PR_2C{\equiv}CR')_2Cl_2$ (M = Ni, Pd, Pt). These reactions, being stereospecific, seem likely to involve an intramolecular cyclization reaction similar to the reactions reported here, at least in the sense of the similarity of final products. Mechanistically, our results are probably more closely related to the extensive work by King and several coworkers [5], who report synthesis of a large number of polyphosphines by base-catalyzed addition reactions. However, there are differences between the two systems. Here, very mild conditions are required and since the reactions involved phosphines locked in a specific configuration with respect to a metal center they offer the possibility for template-type syntheses of polyphosphine ligands not accessible through other routes. Macrocyclic phosphine ligands are of some significance, having been first reported only recently [6,7]. In addition it is important to note that there

is, apparently, a limitation in the scope of this reaction. At least in the results to date the electronic and possibly steric features of the acetylene substituent groups appear to dictate whether success or failure will result. This point obviously needs additional study, and we are directing further efforts to this problem.

Acknowledgement

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