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Synthesis and Reactions Involving the Phosphine Ligands of Bis(phosphine)chromium and -Molybdenum Tetracarbonyl Compounds

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Synthesis of the compounds $M(CO)_4(PPh_2H)(PPh_2R)$ *(*$M = Cr, Mo$*;* $R = CH_2CH{=}CH_2$, $CH_2C(CH_3){=}CH_2$, $CH_2CH{=}CHCH_3$, $CH_2CH{=}CHPh$*) is accomplished from the reaction of the appropriate allyl or substituted allyl chloride with* $[M(CO)_4(PPh_2H)PPh_2]^-$*. This latter reagent is generated* in situ *from* $M(CO)_4(PPh_2H)_2$ *and one equivalent of BuLi in THF. Addition of 2,2'-azobis(isobutylnitrile) (AIBN), a free radical catalyst, to* $M(CO)_4(PPh_2H)(PPh_2CH_2CH{=}CH_2)$ *causes the P–H unit to add to the allylic double bond, giving* $M(CO)_4(Ph_2PCH_2CH_2CH_2PPh_2)$ *(*$M = Mo, Cr$*). The compounds* $M(CO)_4(PPh_2H)(PPh_2CH{=}CH_2)$*, not accessible by the route above, can be made by the reaction of* $[M(CO)_4(PPh_2H)Cl]^-$ *and* $PPh_2CH{=}CH_2$ *in the presence of* $AgNO_3$*. Addition of base (PhLi) causes the cyclization of the phosphine ligands in these compounds, giving* $M(CO)_4(Ph_2PCH_2CH_2PPh_2)$*.*

Introduction

Recently [1, 2] we reported the synthesis of metal complexes of chelating diphosphines via base catalyzed additions of metal complexes of secondary phosphines, vis:

$$cis\text{-}Cr(CO)_4(PPh_2H)_2 + RC{\equiv}CR' \rightarrow cis\text{-}Cr(CO)_4(PPh_2CHRCHR'PPh_2)$$

A sequence of several steps accounts for these products. Initially, deprotonation of one phosphine occurs generating a metal phosphide complex; this can then add to the acetylene to give a carbanion which abstracts a proton from the second phosphine. Intramolecular cyclization can then occur by addition of the coordinated phosphido group to the vinyl group of the coordinated vinylphosphine, with protonation yielding the final product. Both steps, involving phosphide additions to an unsaturated carbon unit, generate stabilized carbanions; thus, this reaction can be considered to be a type of Michael reaction.

For the work reported in this paper, the second step of this reaction is of interest. If the mechanism proposed is correct then it should be possible to cause intramolecular cyclization of P–H and $P{-}CH{=}CH_2$ groups in compounds such as $M(CO)_4(PPh_2H)(PPh_2CH{=}CH_2)$, presuming the ligands are in *cis*-configurations. Further extension of this work to other metal complexes in which P–H (or other X–H units) and $>C{=}C<$ units are incorporated into different ligands is also conceivable; the success of such template reactions would strongly assist the eventual synthesis of unusual polydentate ligands. This paper describes initial results in this area.

In order to carry out this study it was first necessary to synthesize various new metal complexes with two different phosphines. The routes by which this was done are also described.

Experimental

All reactions were carried out under nitrogen. Tetrahydrofuran was distilled from $LiAlH_4$ and diglyme was distilled from CaH_2; other reagent grade solvents were used as obtained. Acid washed Merck alumina was used in the chromatographic separations. The compounds PPh_2H [3], $PPh_2CH{=}CH_2$ [4], $[Et_4N][M(CO)_5Cl]$ [5], and $M(C_7H_8)(CO)_4$ [6] ($M = Cr, Mo$) were prepared according to literature procedures. The synthesis of $M(CO)_4(PPh_2H)_2$ compounds from $M(C_7H_8)(CO)_4$ and PPh_2H is described below.

Melting points were determined using a Thomas–Hoover capillary melting point apparatus and are uncorrected. Infrared spectra using KBr pellets were recorded on a Perkin–Elmer 457 Grating Spectrometer. High resolution mass spectra were recorded on an AEI MS-9 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

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Preparation of cis-$Cr(CO)_4(PPh_2H)_2$

To a solution of 3.55 g (10.9 mmol) $Cr(C_7H_8)(CO)_4$ in 50 ml of 1:3 Et_2O/hexane was added ~5 ml (~28 mmol) PPh_2H. The reaction mixture was refluxed for 3 hr. The solution was cooled to room temperature, filtered, and chilled to −21°; at this temperature the pale yellow crystalline product precipitated out. This was filtered and dried, and could be recrystallized from the same solvent mixture, mp. 130–2 °C (yield: 6.6 g, 89%).

Anal. Calcd. for $C_{28}H_{22}P_2O_4Cr$: C, 62.3; H, 4.11; P, 11.5%. Found: C, 62.45; H, 4.10; P, 11.30%. ν(CO) 2008s, 1910s, 1892s, 1970s cm^{-1}.

Preparation of cis-$Mo(CO)_4(PPh_2H)_2$

The procedure described above was used to prepare this white crystalline product in 82% yield, mp. 110–112 °C.

Anal. Calcd. for $C_{28}H_{22}P_2O_4Mo$: C, 56.1; H, 3.70; P, 10.35%. Found: C, 56.05; H, 3.65; P, 10.20%. ν(CO) 2020s, 1920s, 1900vs, 1870vs cm^{-1}.

Preparation of cis-$Cr(CO)_4(PPh_2H)(PPh_2CH_2CH_2CH{=}CH_2)$

A solution of 0.58 g (1.07 mmol) of $Cr(CO)_4(PPh_2H)_2$ in 30 ml of THF at room temperature was treated with 0.50 ml of 2.0 *M* n-BuLi (1.0 mmol). After stirring for 10 min the resulting orange solution was treated with 0.30 g (4.0 mmol) of $CH_2{=}CHCH_2Cl$. The solution gradually became green. After stirring for an additional 30 min the solution was evaporated to dryness. The residue was re-dissolved in benzene, and this solution was filtered through 1.5 cm of alumina. The filtrate was reduced to a volume of about 2 ml and chromatographed. Elution with benzene gave a green band which gave a green oil after removal of the solvent. The green oil was dissolved in a chloroform-hexane mixture, and the solution cooled, giving 0.35 g (60% yield) of *cis*-$Cr(CO)_4(PPh_2H)(PPh_2CH_2CH{=}CH_2)$ as green crystals; mp. 118–120 °C.

Anal. Calcd. for $C_{31}H_{26}O_4P_2Cr$: C, 64.59, H, 4.55, P, 10.75%. Found: C, 64.51, H, 4.65, P, 10.76%; Mol. wt. 576 (mass spect.). ν(CO) 2008s, 1908s, 1892s, 1868vs cm^{-1}.

The following compounds were prepared by a similar procedure:

cis-$Cr(CO)_4(PPh_2H)(PPh_2CH_2CH{=}CHCH_3)$

Prepared in 66% yield, crystallized from dichloromethane–pentane on slow evaporation; mp. 77–79 °C.

Anal. by parent peak match in mass spec. Found: 590.08587. Calcd. $^{12}C_{32}{}^{1}H_{28}{}^{16}O_4{}^{31}P_2{}^{52}Cr$: 590.08678. ν(CO) 2006s, 1913s, 1898vs, 1869vs cm^{-1}.

cis-$Cr(CO)_4(PPh_2H)(PPh_2CH_2C(CH_3){=}CH_2)$

Obtained as green crystals, 54% yield, from dichloromethane–pentane; mp. 110–111 °C.

Anal. by parent peak match in mass spec. Found: 590.08587. Calcd. $^{12}C_{32}{}^{1}H_{28}{}^{16}O_4{}^{31}P_2{}^{52}Cr$: 590.08678. ν(CO) 2006s, 1913s, 1898vs, 1869vs cm^{-1}.

cis-$Cr(CO)_4(PPh_2)(PPh_2CH_2CH{=}CHPh)$

Green crystals, obtained in 61% yield, recrystallized from dichloromethane–pentane; mp. 150–152 °C.

Anal. Calcd. for $C_{37}H_{30}O_4P_2Cr$: C, 68.09; H, 4.63; P, 9.49%. Found: C, 68.29; H, 4.86; P, 9.58%; Mol. wt. 652 (mass spec.). ν(CO) 2008s, 1928s, 1898vs, 1880vs cm^{-1}.

Preparation of cis-$Mo(CO)_4(PPh_2H)(PPh_2CH_2CH{=}CH_2)$

A solution of 0.58 g $Mo(CO)_4(PPh_2H)_2$ (0.97 mmol) in 30 ml THF was treated with an equimolar amount of n-BuLi at room temperature. The resulting orange solution was stirred for 15 min and then treated with 0.40 g (~5 mmol) of $CH_2{=}CHCH_2Cl$. The orange solution gradually turned light yellow. After stirring for an addition 30 min the solution was evaporated to dryness, redissolved in benzene, and filtered through 1.5 cm of alumina. The filtrate was reduced to a volume of about 2 ml and this material was chromatographed on alumina. Elution with benzene gave an orange band which gave an orange oil upon removal of the solvent. Crystallization of the orange oil in a diethyl ether-pentane mixture gave 0.40 g (65% yield) of this product as white crystals; mp. 104–106 °C.

Anal. by parent peak match in mass spec. Found: 622.03581. Calcd. $^{12}C_{31}{}^{1}H_{26}{}^{16}O_4{}^{31}P_2{}^{98}Mo$: 622.03663. ν(CO) 2018s, 1918s, 1900vs, 1870vs cm^{-1}.

The following compounds were prepared by a similar procedure:

cis-$Mo(CO)_4(PPh_2H)(PPh_2CH_2CH{=}CHCH_3)$

White crystals, obtained in 72% yield, mp. 74–75 °C.

Anal. by parent peak match in mass spec. Found: 636.05149. Calcd. $^{12}C_{32}{}^{1}H_{28}{}^{16}O_4{}^{31}P_2{}^{98}Mo$: 636.05226. ν(CO) 2020s, 1920s, 1905vs, 1866vs cm^{-1}.

cis-$Mo(CO)_4(PPh_2H)(PPh_2CH_2C(CH_3){=}CH_2)$

White crystals, obtained in 69% yield; mp. 112–113 °C.

Anal. by parent peak match in mass spec. Found: 636.05322. Calcd. $^{12}C_{32}{}^{1}H_{28}{}^{16}O_4{}^{31}P_2{}^{98}Mo$: 636.05226. ν(CO) 2020s, 1920s, 1902vs, 1874vs cm^{-1}.

cis-*Mo(CO)$_4$(PPh$_2$H)(PPh$_2$CH$_2$CH=CHPh)*

White crystals, obtained in 72% yield; decomp. 147 °C without melting.

Anal. by parent peak match in mass spec. Found: 698.06684. Calcd. $^{12}C_{37}{}^{1}H_{30}{}^{16}O_4{}^{31}P_2{}^{98}Mo$: 698.06792. ν(CO) 2020s, 1934s, 1903vs, 1888vs cm^{-1}.

Preparation of cis-*Et$_4$N[Cr(CO)$_4$(PPh$_2$H)Cl]*

This product was prepared using a modification of the literature [7] preparation of other Et$_4$N[Cr(CO)$_4$(L)Cl] compounds. To 2.6 g (7.2 mmol) of Et$_4$N[Cr(CO)$_5$Cl] in 50 ml diglyme was added 1.4 g (7.5 mmol) of PPh$_2$H. While stirring at room temperature, the reaction was monitored by the ν(CO) absorptions (product ν(CO) at 2001m, 1890s, 1873s, sh, 1816s). After 2 hr, the solution was filtered. Enough pentane was added to the filtrate to initiate precipitation. The yellow precipitate was filtered, washed with pentane, and dried under vacuum. Et$_4$N[Cr(CO)$_4$(PPh$_2$H)Cl] (1.2 g, 30% yield) was obtained as yellow powder; this was used immediately in subsequent experiments. Analyses were not obtained owing to the instability of this compound. The product rapidly decomposed thermally, and was also air sensitive.

Preparation of cis-*Cr(CO)$_4$(PPh$_2$H)(PPh$_2$CH=CH$_2$)*

A 0.50 g sample (2.3 mmol) of PPh$_2$CH=CH$_2$ and 0.40 g AgNO$_3$ (2.3 mol) were dissolved in 50 ml of a 2:1 THF/H$_2$O mixture. To this was added a solution of 1.2 g (2.3 mmol) of Et$_4$N[Cr(CO)$_4$(PPh$_2$H)Cl] in 30 ml THF; precipitation of AgCl occurred immediately. After 30 min the solution was filtered and the filtrate evaporated. The residue left from evaporation was then extracted with CHCl$_3$; this solution was dried over MgSO$_4$, filtered, and then the solvent removed. The residue was dissolved in benzene and chromatographed on alumina. Elution with benzene gave a green band which upon evaporation gave a green oil. Crystallization from a benzene–pentane mixture gave 0.61 g (50% yield) of the green crystalline product; mp. 137–139 °C.

Anal. Calcd. for $C_{30}H_{24}O_4P_2Cr$: C, 64.06; H, 4.30; P, 11.01%. Found; C, 63.67; H, 4.22; P, 11.23%; mol. wt. 562 (mass spec). ν(CO) 2008s, 1918s, 1898vs, 1864vs cm^{-1}.

Preparation of cis-*Et$_4$N[Mo(CO)$_4$(PPh$_2$H)Cl]*

A sample of Et$_4$N[Mo(CO)$_5$Cl] (3.0 g, 7.3 mmol) was dissolved in 50 ml diglyme and 1.4 g (7.5 mmol) PPh$_2$H was added. As with the analogous chromium system, the reaction, run at room temperature, was monitored by infrared (product ν(CO) at 2010m, 1896s, 1878s, sh, 1818s). After 1.5 hr the solution was filtered. Enough pentane was added to the filtrate to cause precipitation. The resulting yellow powder was filtered, washed with pentane, and dried under vacuum (2.6 g, 64% yield). As with the chromium compound, unstability prevented further characterization and the compound was used immediately in the next reaction.

Preparation of cis-*Mo(CO)$_4$(PPh$_2$H)(PPh$_2$CH=CH$_2$)*

This reaction was carried out in a manner identical to that used to prepare the chromium analogue. The light yellow band from the chromatographic step was evaporated to an oil which crystallized in a diethyl ether–pentane mixture as white crystals in 64% yield; mp. 128–130 °C.

Anal. Calcd. for $C_{30}H_{24}O_4P_2Mo$: C, 59.41; H, 3.99; P, 10.21%. Found: C, 59.22; H, 4.04; P, 10.13%. mol. wt., 608 (mass spec, ^{98}Mo). ν(CO) 2018s, 1930s, 1898vs, 1870vs cm^{-1}.

Phenyllithium Promoted Cyclization Reaction of cis-*Cr(CO)$_4$(PPh$_2$H)(PPh$_2$CH=CH$_2$)*

A 0.40 g sample of cis-Cr(CO)$_4$(PPh$_2$H)(PPh$_2$CH=CH$_2$) (0.71 mmol) was dissolved in 30 ml THF and 0.36 ml of 2 *M* PhLi (0.72 mmol) added. The solution immediately turned orange. After stirring 2 hr at room temperature, 2 ml of 6 *M* HCl was added. After an additional 15 min the solvent was removed under vacuum. The residue was dissolved in chloroform, dried over MgSO$_4$, and filtered. The filtrate was reduced to a volume of about 2 ml and then chromatographed. Elution with chloroform gave a green band which gave a green oil upon removal of the solvent. Crystallization from a dichloromethane–pentane mixture gave 0.36 g (90% yield) of known Cr(CO)$_4$(Ph$_2$PCH$_2$CH$_2$PPh$_2$) as green crystals. The compound melted at 210–211 °C (lit. [8] mp. 211–212 °C).

Phenyllithium Promoted Cyclization Reaction of cis-*Mo(CO)$_4$(PPh$_2$H)(PPh$_2$CH=CH$_2$)*

This reaction was carried out in the manner described for the analogous chromium compound. The orange solution obtained from CHCl$_3$ elution was evaporated to an oil, and crystallization induced in a dichloromethane–pentane mixture giving the known white crystalline compound in 92% yield; mp. 189–190 °C (lit. [8] mp. 191–193 °C).

None of the compounds, M(CO)$_4$(PPh$_2$H)(PPh$_2$ allyl) (M = Cr, Mo), could be induced to undergo the same reaction. In all cases starting material was recovered from these reactions.

AIBN Promoted Cyclization Reaction of cis-*Cr(CO)$_4$(PPh$_2$H)(PPh$_2$CH$_2$CH=CH$_2$)*

Recent observation [9] of free radical promoted additions of P–H units to olefins prompted this study.

A 0.39 g sample (0.65 mmol) of *cis*-Cr(CO)$_4$(PPh$_2$H)(PPh$_2$CH$_2$CH=CH$_2$) was dissolved in 30 ml benzene and 0.02 g 2,2′-azobis(isobutylnitrile)

(AIBN) was added. After 48 hr reflux the orange solution was filtered. The filtrate was evaporated to a volume of ~2 ml and this was chromatographed on acidic alumina. Elution with benzene gave two green bands. The first green band was evaporated giving a green oil. Crystallization of this oil from a dichloromethane–pentane mixture gave 0.2 g (54% recovery) of the starting material. The second green band was evaporated to give a green oil. Crystallization of the green oil from a benzene–pentane mixture gave 0.05 g (14% yield) of green crystalline $Cr(CO)_4(PPh_2CH_2CH_2CH_2PPh_2)$; mp. 207–209 °C (lit. [10] mp. 206–207 °C).

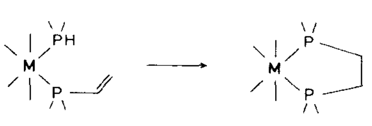
AIBN Promoted Cyclization Reaction of cis-*$Mo(CO)_4(PPh_2H)(PPh_2CH_2CH{=}CH_2)$*

This reaction was run in THF but otherwise resembled the reaction of the chromium analogue. A very small amount of the starting material was obtained. The product, white crystalline $Mo(CO)_4(PPh_2CH_2CH_2CH_2PPh_2)$ was obtained in 48% yield; mp. 189–192 °C (lit. [10] mp. 187–191 °C). Confirmation of the identity of this compound was also obtained using mass spec by parent peak match: Found, 622.03581; Calcd. ${}^{12}C_{31}{}^{1}H_{26}{}^{16}O_4{}^{31}P_2{}^{98}Mo$, 622.03662.

Cyclization reactions using AIBN of the other substituted allylphosphine compounds prepared in this study were also attempted but in each instance only starting material was recovered.

Discussion

As mentioned in the introduction, we recently reported the base promoted reactions of *cis*-$M(CO)_4(PR_2H)_2$ compounds with acetylenes [1, 2]; these reactions gave metal complexes of chelating diphosphines. A mechanism was proposed in this work which incorporated as a second step the addition of the P–H unit of one phosphine ligand to a P–CR=CHR′ of a second phosphine in a *cis* position in the metal coordination sphere, *viz.*:



It seemed reasonable to attempt to support this postulated step by carrying out reactions of this type on metal compounds. This paper reports our efforts in this direction.

For this study it was first necessary to synthesize metal complexes of the general formula $M(CO)_4(L)(L')$, where L and L′ are dissimilar phosphine ligands *i.e.*, L is a secondary phosphine containing an olefinic substituent group. Looking broadly at this problem we elected to allow L′ to be either a vinyl or allylphosphine. These compounds were prepared in favorable yields by the following reactions:

Method 1

$$M(CO)_4(PPh_2H)_2 \xrightarrow{\text{1 equiv. BuLi}} [M(CO)_4(PPh_2H)(PPh_2)]^- \xrightarrow{RCl} M(CO)_4(PPh_2H)(PPh_2R)$$

$$(M = Cr, Mo; R = CH_2CH{=}CH_2, CH_2C(CH_3){=}CH_2, CH_2CH{=}CHCH_3, CH_2CH{=}CHPh)$$

Method 2

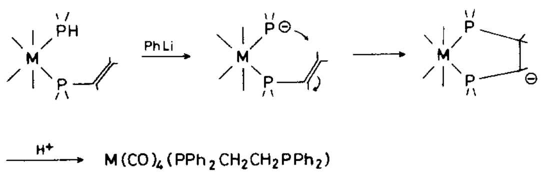
$$Et_4N[M(CO)_5Cl] \xrightarrow{PPh_2H} Et_4N[M(CO)_4(PPh_2H)Cl] \xrightarrow[AgNO_3]{PPh_2CH=CH_2} M(CO)_4(PPh_2H)(PPh_2CH{=}CH_2)$$

$$(M = Cr, Mo)$$

Method 1 involved initial deprotonation of one of the phosphines followed by reaction of the phosphido–metal complex with an allyl halide. This type of reaction, nucleophilic halide replacement, has a suitable precedence in previous work [11, 12]. However it is significant that the reaction can be controlled by choice of stoichiometry, so that mono-deprotonation and mono-alkylation can be accomplished specifically. Method 2 begins with the known reaction [7] of $[M(CO)_5Cl]^-$ with phosphines to give, specifically, $Et_4N[M(CO)_4(phos)Cl]$. In this work $Et_4N[M(CO)_4(PPh_2H)Cl]$ was prepared. This compound, which proved difficult to handle, reacted with $PPh_2CH{=}CH_2$ in the presence of $AgNO_3$ to give the desired product. This presence of $AgNO_3$ in the second step deserves specific note. In the previous work [7] an unsuccessful attempt had been made to prepare $M(CO)_4(L)(L')$ compounds from $[M(CO)_4(L)Cl]^-$ and L′ by thermal reactions, but apparently mixtures of products were obtained. The addition of a halide acceptor, Ag^+, allows this reaction to be run at lower temperature with a greatly increased selectivity to the desired product.

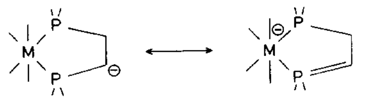
While the complexes $M(CO)_4(PPh_2H)(PPh_2R)$ (R = allyl, substituted allyl) could probably have been made by Method 2, the convenience of Method 1 dictated its use. The compounds $M(CO)_4(PPh_2H)(PPh_2CH{=}CH_2)$ could not be made by Method 1 owing to the low reactivities of vinyl halides to nucleophilic halide displacement.

Addition of one equivalent base (PhLi) to a THF solution of $M(CO)_4(PPh_2H)(PPh_2CH{=}CH_2)$ caused immediate deprotonation of the secondary phosphine. The phosphido complex then underwent a rapid internal cyclization, and protonation gave the products $M(CO)_4(PPh_2CH_2CH_2PPh_2)$ in high yields (~90%).



This result would thus appear to be in accord with our earlier mechanistic hypotheses concerning the $M(CO)_4(PPh_2H)_2$ plus acetylene reactions for which a similar reaction is suggested.

It is interesting to note that addition of PhLi to the $M(CO)_4(PPh_2H)(PPh_2allyl)$ compounds prepared here did not lead to a similar cyclization reaction. This is not surprising however, for the basis for this type of reaction (Michael reaction) is the formation of a stabilized carbanion intermediate. In the initial product arising from addition using the vinyl phosphine the carbanion site is adjacent to a phosphorus atom and the negative charge can be stabilized by delocalization to metal and carbonyls as shown below:



In contrast such stabilization is not accorded to the product of addition to an allyl group where the negative charge would end up one carbon removed from phosphorus.

Failing to effect a base catalyzed cyclization of phosphine ligands in the latter case we attempted to cause this reaction by addition of a free radical initiator (AIBN). In the cases of $M(CO)_4(PPh_2H)(PPh_2CH_2CH{=}CH_2)$ cyclization was achieved, *viz.*:

$$M(CO)_4(PPh_2H)(PPh_2CH_2CH{=}CH_2) \xrightarrow{\text{AIBN}} M(CO)_4(PPh_2CH_2CH_2CH_2PPh_2)$$

(M = Mo, Cr)

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