

## REDUCTIVE ELIMINATION OF DIHYDROGEN FROM ARENECHROMIUM DIMERS

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### Summary

Biphenylbis(chromium dicarbonyl)- $\mu$ -bis(diphenylphosphido)methane and its arsenic analog have been prepared in good yield by UV irradiation of biphenylbis(chromium tricarbonyl) and bis(diphenylphosphido)methane or bis(diphenylarsino)methane in benzene. Addition of strong acid to these dinuclear compounds results in rapid dihydrogen evolution and subsequent decomposition of the oxidized chromium species. A scheme for the dihydrogen elimination reaction is proposed in which both metal centers are protonated in an oxidative addition step, followed by reductive elimination of dihydrogen from the two metal centers.

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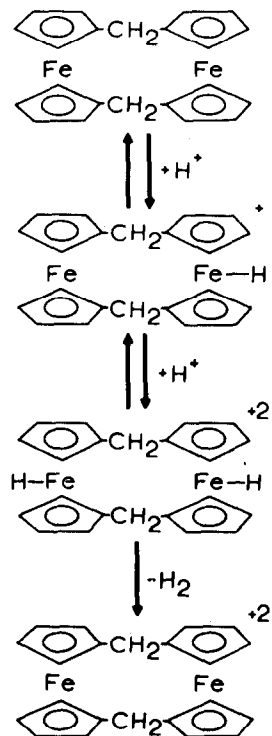
During the course of an extended study of ferrocene protonation in very strong acids, we examined a series of dinuclear ferrocenes in order to see if protonation at one metal center would suppress protonation at a second center [1]. The  $^1\text{H}$  NMR spectra of these dinuclear ferrocenes in trifluoroboric acid,  $\text{HBF}_3\text{OH}$ , demonstrated that protonation occurred at both metal centers. Unlike the mononuclear compounds which we had studied [2,3,4], these protonated, dinuclear species oxidized in solution during the time necessary for the recording of the NMR spectra. The rate of oxidation was found to be dependent upon the separation of the ferrocenyl moieties. For the series,  $\text{Fc}(\text{CH}_2)_n\text{Fc}$ , where  $\text{Fc}$  = ferrocenyl and  $n = 1,2,3$ , the rate of oxidation was found to increase as  $n$  decreased.

Addition of trifluoroboric acid to [1.1]ferrocenophane resulted in instantaneous oxidation and evolution of a gas shown to be dihydrogen. It is now believed that all of the dinuclear ferrocenes oxidize with concurrent dihydrogen evolution, and that the rate of the reaction is dependent upon the likelihood that the two protonated metal centers can approach one another.

The mechanism which was suggested for this reaction is shown in Scheme 1. If the iron atoms in the parent ferrocenophane are considered to be iron(II), then protonation can be formally considered to be an oxidative addition creating an iron(IV) hydride. Interaction of a pair of iron(IV) hydrides results in loss of dihydrogen and

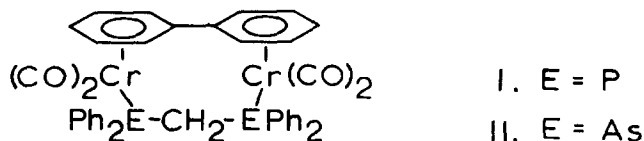
reduction of the iron(IV) to iron(III). Thus dihydrogen evolution constitutes a unique example of reductive elimination involving two metal centers.

Numerous other metal complexes are known to undergo protonation at the metal



so it was of interest to determine whether reductive elimination of dihydrogen might be a general reaction for protonated dimers of these metal complexes. For example, metal-protonation of arenechromium tricarbonyl complexes have been studied by several groups [5-11].  $^1\text{H}$  NMR and IR studies have shown that the metal-protonation is complete in very strong acids such as trifluoroboric acid and fluorosulfonic acid, but no chromium-bound hydrogen is observed in trifluoroacetic acid. Substitution of a triphenylphosphine for a carbonyl on the chromium enhances the metal basicity so that arenechromium dicarbonyltriphenylphosphine derivatives were found to be completely protonated in trifluoroacetic acid [8,9,10]. The stereochemical nonrigidity of protonated arenechromium dicarbonylphosphines has been studied by Flood and his coworkers [11].

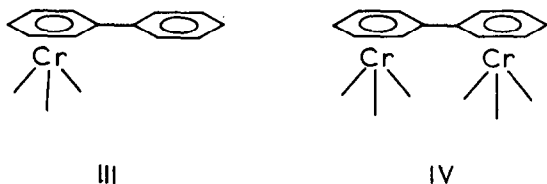
In order to test the possibility that reductive elimination of dihydrogen might be a general reaction of basic dinuclear metal derivatives, we undertook the synthesis of a pair of dinuclear arenechromium carbonyls I and II. The results of these syntheses and the subsequent studies in acid media are reported in this paper.



## Synthesis

$^1\text{H}$  and  $^{31}\text{P}$  NMR data and IR carbonyl stretching frequencies of compounds discussed in the text are included in Table 1. In several cases, decomposition or rearrangement was observed during purification attempts. In the cases of those compounds known to be impure, IR spectra and  $^1\text{H}$  NMR spectra were not recorded. Mass spectral fragmentation data for compounds I and II are presented in Table 2.

Biphenylchromium tricarbonyl, III, and biphenylbis(chromium tricarbonyl), IV,



were prepared by the method of Top and Jaouen [12]. Substitution of a phosphine or arsine for carbon monoxide was achieved by ultraviolet irradiation of benzene solutions of the chromium species and the phosphine or arsine as described by Strohmeier [13].

Semmelhack and his coworkers have recently reported the results of a study of the reaction of benzenechromium tricarbonyl and bis(diphenylphosphino)ethane, diphos [14]. Following irradiation in benzene, these workers isolated two species containing chromium bound diphos from the reaction mixture. These products were examined by  $^1\text{H}$  and  $^{31}\text{P}$  NMR and IR and were assigned to the structures V and VI. The chelated species, VII, was not observed in this reaction.

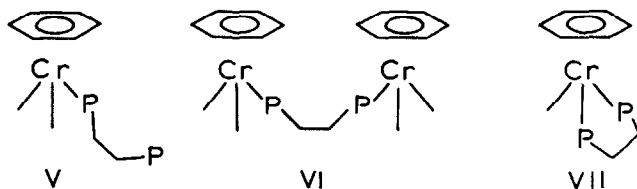
TABLE 1  
SPECTRAL DATA

Compound	$^1\text{H}$ NMR <sup>a,b</sup>	$^{31}\text{P}$ NMR <sup>b,c</sup>	IR <sup>d,e</sup>
I	6.83(4), 6.14(2), 5.31(4)	76.76	1883, 1835
II	6.79(4), 6.09(2), 5.24(4)	—	1888, 1830
III	4.86(2), 4.43(3)	—	1970, 1900
IV	4.71–4.33(m)	—	1970, 1900
V	4.22(m)	85.1(br s), –12.4(br s)	1884, 1806
VI	4.51(m)	85.1	1883, 1823
VIII	— <sup>f</sup>	82.57(d), –26.11(d) <i>J</i> 63.4 Hz.	1882, 1823
IX	— <sup>f</sup>	85.82	— <sup>f</sup>
X	— <sup>f</sup>	21.50	— <sup>f</sup>
XI	— <sup>f</sup>	82.44(d), –26.20(d) <i>J</i> 62.5 Hz.	— <sup>f</sup>
XII	— <sup>f</sup>	85.75	— <sup>f</sup>
XIII	— <sup>f</sup>	71.03	1886, 1825
XIV	5.15(2), 4.89(3)	90.43	1890, 1832
XV	5.20(2), 4.83(3)	—	1896, 1835

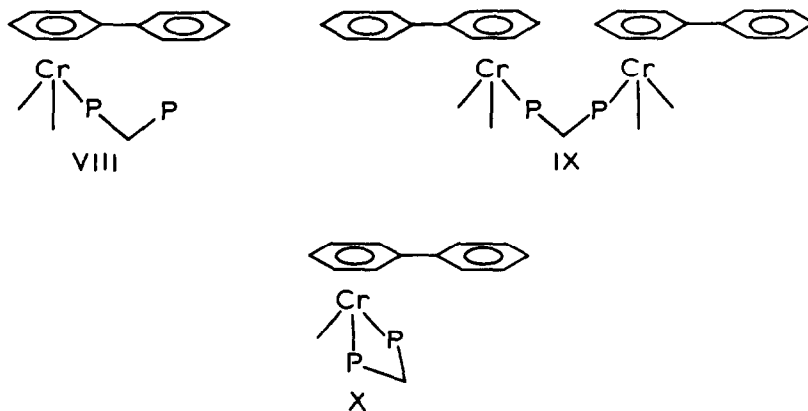
<sup>a</sup> Chromium-bound arene protons. <sup>b</sup>  $\text{C}_6\text{D}_6$  solvent. <sup>c</sup> Relative to 85%  $\text{H}_3\text{PO}_4$ . <sup>d</sup>  $\text{DCCl}_3$  solvent. <sup>e</sup> Carbonyl stretching frequencies ( $\text{cm}^{-1}$ ). <sup>f</sup> Pure compound could not be obtained.

TABLE 2  
MASS SPECTRAL FRAGMENTATION DATA

Fragment	Compound I	Compound II
$M^+$	754(0.12)	—
$M^+ - \text{CO}, \text{C}_6\text{H}_5\text{P}$	614(0.13)	—
$M^+ - \text{C}_{12}\text{H}_{10}$	600(0.33)	—
$M^+ - \text{Cr}(\text{CO})_4$	590(0.49)	—
$M^+ - \text{C}_{12}\text{H}_{10}, 2\text{CO}$	544(2.0)	6.33(0.04)
$(\text{CO})_2\text{Cr}(\text{dpem})$	492(5.7)	581(1.4)
$M^+ - \text{C}_{12}\text{H}_{10}, 4\text{CO}$	488(2.3)	—
$(\text{CO})\text{Cr}(\text{dpem})$	464(0.31)	—
$\text{Cr}(\text{dpem})$	436(100)	525(14.4)
$\text{C}_{12}\text{H}_{10}[\text{Cr}(\text{CO})_3]_2$	426(1.2)	426(1.10)
$\text{dpem}$	384(6.93)	472(100)
$\text{C}_{12}\text{H}_{10}[\text{Cr}(\text{CO})_2]_2$	370(0.5)	—
$\text{C}_{12}\text{H}_{10}\text{Cr}_2(\text{CO})_3$	342(2.8)	432(0.55)
$\text{C}_{12}\text{H}_{10}(\text{CrCO})_2$	314(13.5)	314(0.4)
$\text{C}_{12}\text{H}_{10}\text{Cr}(\text{CO})_3$	290(6.44)	290(9.59)
$\text{C}_{12}\text{H}_{10}\text{Cr}_2\text{CO}$	286(3.25)	286(1.4)
$(\text{C}_6\text{H}_5)_3\text{E}$	262(44.2)	306(58.9)
$\text{C}_{12}\text{H}_{10}\text{Cr}(\text{CO})_2$	262(44.2)	262(0.55)
$\text{C}_{12}\text{H}_{10}\text{CrCO}$	234(11.7)	234(7.8)
$\text{C}_{12}\text{H}_{10}\text{Cr}$	206(33.1)	206(34.3)

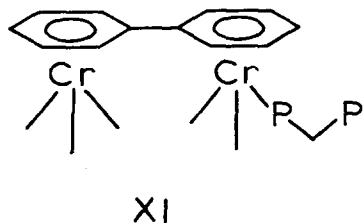


Reaction of III with bis(diphenylphosphino)methane, dppm, was found by HPLC to produce three products. Two of these could be recovered by column chromatography, but the third, a slow moving yellow band, decomposed on the column. The  $^{31}\text{P}$  NMR spectra of the two recovered compounds indicate that one of the compounds has a dppm ligand bound at only one phosphorus atom, while the dppm of the second compound is bound at that both ends. The metal bound phosphorus resonances of these two compounds both fall at 85.10 ppm. By comparison, the  $^{31}\text{P}$  NMR chemical shifts of biphenylchromium dicarbonyldiphenylmethylphosphine, XIII, and biphenylchromium dicarbonyltriphenylphosphine, XIV, fall at 71.03 ppm and 90.43 ppm, respectively. The two recovered compounds are believed to be analogous to the compounds isolated by Semmelhack and his coworkers and have been assigned the structures VIII and IX. A  $^{31}\text{P}$  NMR singlet resonance at 21.50 ppm is observed in the spectrum of the reaction mixture. Since this singlet falls well below the region expected for nonchelating dppm ligands in these compounds, we have tentatively assigned it to the unrecovered third band, which we believe to be the chelated species, X [15]. Further attempts to recover this compound are in progress. It should be noted that attempts to purify these compounds for elemental analysis were frustrated by decomposition and rearrangement during the purification pro-

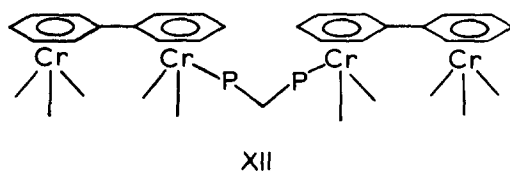


cess. A similar problem was reported by Semmelhack and his coworkers [14].

Reaction of IV with dppm yielded four isolable compounds containing chromium-bound dppm.  $^{31}\text{P}$  NMR spectra of the reaction mixture indicated the presence of compounds with chemical shifts around 20 ppm which probably contain chelated dppm ligands, but these compounds could not be recovered from the reaction mixture. Of the isolated compounds, two were found by  $^{31}\text{P}$  NMR to contain singly attached dppm ligands. One of these was shown by  $^{31}\text{P}$  NMR and HPLC to be identical to VIII, and presumably results from the loss of a chromium tricarbonyl fragment during irradiation. Substantial quantities of III were also found in the reaction mixture indicating that loss of a chromium tricarbonyl moiety during irradiation is a relatively common pathway for these compounds. A second compound containing a singly attached dppm ligand was isolated in small amounts and could not be purified. It is assigned the structure XI. The two remaining compounds



each showed only one phosphorus resonance in the chromium-dppm region. One of these was isolated in trace amounts and could not be purified. It is tentatively assigned structure XII. The remaining compound, which constituted the major

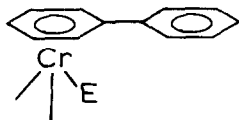


product from the reaction, was shown to be the desired bridged species, I. Nelson and his coworkers have recently reported that irradiation of a dicyclopentadienyldimethylsilanebis(iron carbonyl)dppm dimer with dppm produces a set of

products very similar to those observed here for the dinuclear chromium derivatives [16].

Compound I was recovered from the reaction of IV and dppm in good yield. Recrystallization from benzene/ligroin yields orange-red crystals. The  $^{31}\text{P}$  NMR spectrum of this material in benzene was characterized by a single, sharp resonance in the chromium-dppm region. The  $^1\text{H}$  NMR spectrum contains a well resolved resonance pattern in the arenechromium region characteristic of a symmetric biphenyl. The biphenyl *o*-, *m*-, and *p*-ring protons are located at 6.83, 6.14 and 5.31 ppm, respectively, as compared to the biphenyl protons in the spectrum of IV which appear as a broad multiplet between 4.71 and 4.33 ppm. The IR spectrum of this compound in chloroform shows two strong carbonyl absorbances with exactly the same frequencies as observed for compound VIII. The mass spectrum of this compound has a small parent mass at 754 mass units and a fragmentation pattern shown in Table 2, which is reasonable for the proposed structure. Elemental analysis was satisfactory. This evidence strongly supports the assignment of the bridged structure, I, to the major product.

Reaction of IV with bis(diphenylarsino)methane, dpam, yielded a red-orange compound as the major product. The  $^1\text{H}$  NMR spectrum of this compound contains a symmetric biphenyl pattern identical to that observed for I. The IR spectrum of this compound has two strong carbonyl absorptions close to those observed for I. It should be noted that the related compounds biphenylchromium dicarbonyltriphenylphosphine, XIV, and biphenylchromium dicarbonyltriphenylarsine, XV, have almost



XIII. E =  $\text{PPh}_2\text{Me}$

XIV. E =  $\text{PPh}_3$

XV. E =  $\text{AsPh}_3$

identical metal carbonyl stretching frequencies. The mass spectrum of the dpam compound does not show a parent mass, but the fragmentation pattern, shown in Table 2, is similar to that of I. The elemental analysis of this compound is consistent with its being the arsenic analog of I.

HPLC analysis of the reaction mixture of IV and dpam indicates that the reaction mixture contains several products in addition to II. In the absence of a convenient spectral handle to characterize these compounds, no attempt was made to recover them.

### Dihydrogen evolution reactions

As noted in the Introduction, arenechromium tricarbonyl complexes are weakly basic and require very strong acids for complete protonation. Substitution of a phosphine for a carbonyl increases the basicity permitting complete protonation in trifluoroacetic acid. For this reason, it was anticipated that trifluoroacetic acid might be an effective medium for dihydrogen evolution studies. Unfortunately, neither

compound I nor II proved to be soluble in this acid.

Addition of thoroughly degassed trifluoroboric acid or fluorosulfonic acid to compounds I and II resulted in the immediate liberation of gas. The acid solution of I was brown for several minutes, then slowly turned deep blue. Acid solutions of II darkened and turned blue almost immediately after acid addition. Mass spectral analysis of the gases in the reaction flask confirmed that dihydrogen was present in the reaction flask after mixing. A volumetric measurement of gas evolution was conducted using fluorosulfonic acid, which has a low vapor pressure, as the reactant acid. It was found that one mole of gas per mole of dimer is liberated within minutes of the addition of acid to either compound I or II. Gas evolution does not cease at this point, but instead continues at a steadily decreasing rate for several hours. After three hours a total of about three moles of gas per mole of dimer were collected.

Mass spectral analysis of the gas formed in the first few minutes of the reaction shows it to contain dihydrogen. Samples taken from the reaction flask after about ten minutes indicate that a species with a mass of 28 is also present in the gas phase. Since there is no concurrent increase in ions which might be associated with dioxygen or dinitrogen, it is believed that this second gas is carbon monoxide. Deuterated acids react with compounds I and II to generate mixtures of  $H_2$ , HD, and  $D_2$ . The relative distributions of these components is indicated in Table 3.

In order to determine the identity of the products which remain after dihydrogen evolution, a series of reactions between I and trifluoroboric acid were quenched with water at varying times up to fifteen minutes. Extraction of the resulting mixtures with benzene removed all colored components from the water layer, leaving only a small amount of blue-green solid. HPLC and  $^{31}P$  NMR analysis of the recovered benzene soluble mixtures revealed the presence of small amounts of biphenyl and dppm, but showed the major components to be I and VIII. The relative amount of I was found to decrease with increasing time, indicating that the recovered I was either unreacted or perhaps undissolved starting material.

In an independent experiment, VIII was dissolved in trifluoroboric acid to give a stable orange-brown solution. After ten minutes, the solution was quenched with water and the resulting acidic mixture was extracted with benzene. HPLC analysis of the benzene extract showed small amounts of biphenyl and dppm, but most of the chromium compound, VIII, was recovered intact.

Compound II appears to undergo dihydrogen liberation and decomposition in the acids in a manner similar to that of I. Detailed product analysis was not carried out for the reaction of II with acid.

The pattern of the chemistry of the mono- and di-nuclear chromium compounds in acids parallels that of the ferrocene compounds. Mononuclear compounds undergo protonation in strongly acidic media to produce stable, metal-protonated species which can be studied by  $^1H$  NMR and IR. In contrast, addition of acids to

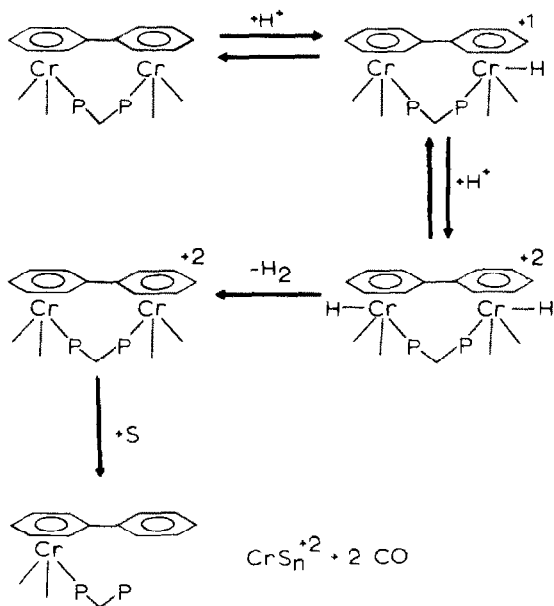
TABLE 3  
REACTIONS WITH DEUTERATED ACIDS

Compound	$H_2$	HD	$D_2$
I	1.5	1.0	2.5
II	1.0	2.0	5.0

the dinuclear compounds results in rapid evolution of dihydrogen.

Facile loss of dihydrogen from the dinuclear iron species  $[(C_5H_5)_2FeH(CO)]_2dppm$  has been recently reported by Davies and his coworkers [17]. Smart and his coworkers [18] have observed that the dinuclear molybdenum complex bisfulvene-bis(hydridomolybdenum tricarbonyl) is much less stable towards loss of dihydrogen and formation of a molybdenum-molybdenum bond than is the monomeric compound.

We believe that the experimental evidence presented above supports a reaction sequence as described in Scheme 2. In this Scheme, a doubly protonated chromium



complex undergoes reductive elimination of dihydrogen leaving a doubly charged intermediate. This intermediate decomposes by disproportionation to give VIII or its arsenic analog and a solvated chromium fragment which is presumably responsible for the blue color of the reaction solutions. The decomposition of the doubly charged product over time accounts for the additional two moles of gas per mole of dimer that are experimentally observed. Presumably addition of water to the acid solutions of I and II during the quenching operations results in the rapid decomposition of the doubly charged species with the formation of VIII and chromium fragments.

The exact nature of the disproportionation reaction of the doubly charged intermediate is not yet known, but it could be triggered by nucleophilic attack of the solvent on one of the chromium centers. Rieke and his coworkers [19] have recently reported on the electrochemical oxidation of several mono- and bis-(chromium tricarbonyl)diaryl complexes and they have noted that the seventeen electron oxidized species are generally unstable to decomposition to an unknown chromium fragment. It is well known that reactions of arenechromium tricarbonyl species with either iodine or cerium(IV) ions will free the arene from the chromium moiety. An electrochemical analysis of the dimer compounds is now in progress directed toward



determining the mechanism of the disproportionation reaction and toward establishing the interaction, if any, between the metal centers.

There remains the possibility that the reactions between I and II and acid might proceed through a totally different mechanism than the one suggested by Scheme 2. For example, protonation of one chromium center might weaken the second chromium-arene bond resulting in separation of the chromium(0) unit from the arene. This pendant chromium(0) species might then react with the acid solution to produce the observed products. While such a process cannot be dismissed, it is difficult to imagine how significant quantities of H<sub>2</sub> and HD might arise from this process in the reactions of I and II with deuterated acids.

Further work on the mechanism of the dihydrogen elimination reaction is in progress in our laboratory.

## Experimental

<sup>1</sup>H and <sup>31</sup>P(<sup>1</sup>H decoupled) spectra were recorded on a Varian FT 80A Spectrometer at room temperature. IR spectra were recorded on a Perkin-Elmer 467 Grating Spectrometer. Mass spectra of compounds I and II were obtained by Dr. Henry Failes and Mr. William Comstock of the National Institutes of Health using an LKB 9000 Mass Spectrometer. Gas samples from the dihydrogen evolution studies were analyzed using a CEC Type 21-621 Mass Spectrometer.

Three chromatographic techniques were used in this work. A Gow-Mac HPLC operating with a Whatman Parasil PXS 10/25 column and 2/1 petroleum ether/tetrahydrofuran was used for analysis of reaction mixtures and to determine product purity. A 15 mm diameter gravity column packed with 100 mesh silica gel was used for bulk separations, and an Altex medium pressure column packed with 40 micron silica gel was used for additional purification of samples recovered by gravity column chromatography. In all cases, chromatographic solvents were flushed with nitrogen before use.

Biphenylchromium tricarbonyl and biphenylbis(chromium tricarbonyl) were prepared by the method of Top and Jaouen [12]. Bis(diphenylphosphino)methane, bis(diphenylarsino)methane, and diphenylmethylphosphine were prepared by literature methods. The preparations of biphenylchromium dicarbonyltriphenylphosphine and its arsenic analog have been presented elsewhere [20]. UV photolysis reactions were conducted in a water-cooled photochemical reactor using a medium pressure Hanovia lamp. All reactions were conducted under high purity nitrogen with deoxygenated solvents. Analyses were conducted by Micro-Analysis, Inc. of Wilmington, DE.

### *Reaction of III and bis(diphenylphosphino)methane*

To a 500 ml photochemical reactor which had been flushed with nitrogen were added 1.0 g (3.5 mmol) of III and 1.32 g (3.5 mmol) of bis(diphenylphosphino)methane. About 250 ml of benzene was transferred to the flask by cannuli. The reaction mixture was irradiated for 12 h during which time the solution changed color from orange to dark red.

After irradiation, the solution was transferred by cannuli into a nitrogen flushed fritted addition funnel and transferred slowly to a vacuum distillation apparatus where the solution was concentrated to about 50 ml. Addition of 100 ml of pentane

failed to produce a crystalline product, so the solvent was completely removed to give a sticky red gum which would not crystallize. This red gum was taken up in 5/100 THF/petroleum ether and placed on a silica gel column. Elution with the same solvent removed a pale yellow foreband containing biphenyl- and bis(diphenylphosphino)-methane followed by a broad orange-red band. A yellow band proceeded slowly down the column but appeared to decompose before it was eluted from the column. HPLC analysis of the broad orange-red band showed it to be composed of two components which were identified by  $^{31}\text{P}$  NMR to be VIII and IX. Repeated chromatography of this mixture on a medium pressure column recovered VIII in about 90% purity. As some of the material was always lost on the column further purification was abandoned. Compound IX could not be obtained in greater than 50% purity.

#### *Reaction of IV with bis(diphenylphosphino)methane*

Using the same procedure described above, 2.0 g (4.7 mmol) of IV and 2.0 g (5.2 mmol) of bis(diphenylphosphino)methane were dissolved in benzene and irradiated for 36 h. Concentration of the reaction mixture to about 50 ml and addition of 50 ml of pentane gave a dark orange solid which was recovered by filtration. Further concentration of the reaction mixture yielded additional crops of the orange solid. Recrystallization of this orange solid from benzene/pentane gave 0.80 g of orange crystals of I, Mp. 205–210°C with decomposition, 22% yield based on IV. The compound appears to crystallize with one benzene of solvation. Analysis: Found: C, 68.09; H, 4.86; P, 6.61.  $\text{C}_{12}\text{H}_{10}[\text{Cr}(\text{CO})_2]_2(\text{C}_6\text{H}_5)_4\text{P}_2\text{CH}_2 \cdot \text{C}_6\text{H}_6$  calcd.: C, 67.79; H, 4.81; P, 7.45%.

Removal of the solvent from the mother liquor gave a gummy red solid which was dissolved in 50/1 petroleum ether/ethyl ether and chromatographed on silica gel with a gravity column. Elution with the same solvent removed first a pale yellow band containing biphenyl and bis(diphenylphosphino)-methane. An orange band containing mostly VIII and III was eluted second, followed by a pale orange band containing III and XI. A final orange band yielded XII contaminated with XI and III. Further attempts to purify compounds XI and XII by medium pressure chromatography were unsuccessful.

#### *Reaction of IV with bis(diphenylarsino)methane*

Following the procedure described above, 2.0 g (4.7 mmol) of IV and 2.28 g (4.7 mmol) of bis(diphenylarsino)methane were dissolved in benzene and irradiated. After transfer and filtration of the reaction mixture, the volume was reduced to 50 ml and 50 ml of pentane was added. The orange-red solid which formed was recovered by filtration. Further concentration of the reaction mixture yielded additional orange-red solid. This material was recrystallized from benzene/pentane to give 2.20 g of orange-red crystals, Mp. 194–195°C, 55% yield based on IV. The compound appeared to crystallize with one benzene of solvation. Analysis: Found: C, 61.98; H, 4.10.  $\text{C}_{12}\text{H}_{10}[\text{Cr}(\text{CO})_2]_2(\text{C}_6\text{H}_5)_4\text{P}_2\text{CH}_2 \cdot \text{C}_6\text{H}_6$  calcd.: C, 61.30; H, 4.34%.

#### *Reactions with acid*

Reactions between the chromium compounds and trifluoroboric acid or fluoro-sulfonic acid were conducted in an apparatus consisting of a three-way adapter to

which a 5.0 ml reaction flask and a 25 ml Schlenk reaction flask were attached. The third joint of the adapter was used to mount either a gas collection flask or to attach the apparatus to a gas burette. Acids were thoroughly deoxygenated before their transfer by syringe to the nitrogen flushed Schlenk flask.

Gas analysis: 100–200 mg of compound I or II were added to the 5.0 ml reaction flask and 2–3 ml of acid were transferred to the Schlenk flask. A 50 ml gas collection flask was attached to the third joint of the three way adapter. The acid was frozen in liquid nitrogen and the apparatus was evacuated. The acid was degassed by three freeze-pump-thaw cycles. During the last freeze cycle, the gas collection flask was isolated from the reaction chamber by closing its stopcock. The acid was warmed to room temperature and transferred to the 5.0 ml flask by tilting the apparatus. Gas evolution was immediate and the reactions were permitted to continue for 3–5 minutes, after which time the reaction flask was immersed in liquid nitrogen and a gas sample taken. The contents of the gas collection flask could be introduced directly to a CEC Model 21-621 Mass Spectrometer for analysis.

Volumetric gas analysis: The apparatus described above was attached to a gas burette and charged with either I or II and fluorosulfonic acid. The reaction apparatus was evacuated and refilled with high purity nitrogen. Gas evolution was monitored from the time of mixing to about 3 h.

Product analysis: 100 mg samples of I were treated with acid, and the reactions were permitted to proceed for 3, 5, 8 and 15 min. The reaction mixtures were quenched with ice water and extracted with benzene. A small amount of blue-green solid was usually observed as a film between the water and benzene layers. The benzene extracts were dried with magnesium sulfate and analyzed by HPLC and  $^{31}\text{P}$  NMR.

A solution of VIII in trifluoroboric acid was prepared. After 10 minutes, the solution was quenched with ice water and extracted with benzene. After drying with magnesium sulfate, the benzene solution was analyzed by  $^{31}\text{P}$  NMR and HPLC.

## Acknowledgements

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