Inorganica Chimica Acta, *172* (1990) 59–64

Effects of Ligand and Metal on the Reductive Elimination of Dihydrogen by Dinuclear Complexes of Chromium and Manganese

THOMAS E. BITTERWOLF*
Department of Chemistry, University of Idaho, Moscow, ID 83843 (U.S.A.)
and KRISHNAN S. RAGHUVEER
Department of Chemistry, Bowling Green State University, Bowling Green, OH 43403 (U.S.A.)

(Received October 26, 1989)

Abstract

Six new dinuclear complexes of the form $(\eta^6,\eta^6\text{-}C_6H_5C_6H_4R)Cr_2(CO)_4\text{-}\mu\text{-}L_2$, where R = H, $L_2 = (CH_3)_4P_2$, $[(CH_3)_2P]_2CH_2$, $[(CH_3O)_2P]_2NCH_3$, $(F_2P)_2NCH_3$, $[(CF_3CH_2O)_2P]_2CH_2$ and R = CH_3, L = $[(C_6H_5)_2P]_2CH_2$ have been prepared and are fully characterized by their elemental analyses and spectral properties. The reactions of several dinuclear chromium compounds and $(\eta^5,\eta^5\text{-}C_5H_4C_5H_4)Mn_2(CO)_4\text{-}\mu\text{-}[(C_6H_5)_2P]_2CH_2$ with strong acids have been examined. Dihydrogen evolution has been observed with all but one of the dinuclear chromium compounds. The relative rate of dihydrogen formation by the chromium compounds was found to be dependent upon the metal basicity which is dictated by the electronic character of the diphosphine ligand. The manganese derivative slowly eliminates dihydrogen under strong acid conditions. Deuterated acids have been shown to react with the dinuclear compounds to liberate mostly, but not exclusively, D_2 suggesting that some hydrogen exchange with either the arene rings or with the ligands is occurring prior to dihydrogen elimination. In no case has it been possible to recover the dinuclear compound intact after the reductive elimination of dihydrogen.

Introduction

Dinuclear reaction centers in which adjacent metal atoms function in a cooperative fashion in the chemical transformation of a ligand are strongly implicated in Fischer-Tropsch chemistry on metal surfaces [1] and may be involved in biochemical processes such as photochemical water splitting [2]. Research in this laboratory has been directed toward the synthesis of basic dinuclear complexes which react with acids to generate dihydrogen via reductive elimination from a protonated species. We seek to optimize this process at the molecular level in expectation that these materials will be of importance in the photocatalytic splitting of water by sunlight. A device based on this principle employing [1.1]ferrocenophane on a semiconductor electrode has been developed by Muller-Westerhoff and Nazzal [3]. Previous work on dinuclear ferrocene compounds [4], diphosphine bridged bis(cyclopentadienyl rhodium carbonyl) methane and fulvalene bis(rhodium carbonyl) complexes [5], and diphosphine and diarsine bridged dinuclear chromium complexes [6], **I** and **II**, have demonstrated that reductive elimination of dihydrogen is most efficient when the two metal atoms are bound in close proximity. Thus a compound such as bis(ferrocenyl)methane in which the ferrocene moieties are free to rotate about the ferrocene–CH_2 bond protonate in acid solutions but only liberate dihydrogen slowly, whereas the analogous [1.1]ferrocenophane liberates dihydrogen rapidly under identical conditions [4].

In order to provide a broader experimental base on which to build a theoretical model we have expanded our earlier investigation of dinuclear chromium compounds to include a variety of diphosphine ligands having both electron donating and withdrawing character and have also examined the reaction of an analogous bicymantrenyl compound. As in the case of the chromium compounds, cyclopentadienylmanganesedicarbonylphosphine compounds have been shown to protonate in strong acid solution [7]. On this basis, it seemed reasonable to prepare a cymantrene dinuclear compound and see whether it reacted to give dihydrogen as the chromium compounds have been shown to do. Reactions with DBF_3OD have been used to establish the source of the hydrogen atoms in the dihydrogen which is produced. The results of these studies support the earlier suggestions of the importance of relative metal–metal geometry and metal basicity in promoting reductive elimination reactions. These observations are discussed in the light of recent electrochemical and structural studies.

---

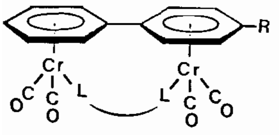
*Author to whom correspondence should be addressed.

0020-1693/90/$3.50

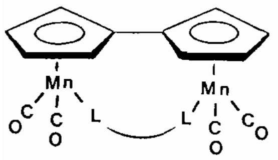
Results and Discussion

Synthesis and Characterization of Chromium and Manganese Dinuclear Complexes

New compounds **III–VIII** were prepared by photolysis of benzene solutions of the appropriate chromium complex and the diphosphine ligand by procedures which have been previously described. A new diphosphite ligand, $[(CF_3CH_2O)_2P)_2CH_2$, employed in the synthesis of **VII** was prepared by reaction of trifluoroethanol with $(Cl_2P)_2CH_2$ and was recovered in good yield as a water white liquid. Compound **IX** was prepared by photolysis of bicymantrene with dppm by a method similar to that recently reported by Herrmann *et al.* [8]. In all cases the compounds were purified by column chromatography and recrystallized from benzene/petroleum ether mixtures to provide analytical samples. In most cases ^{31}P NMR spectra of the reaction mixtures indicated the presence of additional products, notably those containing dangling diphosphine ligands, but no attempt was made to isolate and purify these side products. All compounds were found to be stable in air for brief periods. Some decomposition which appeared to be of a free radical nature was observed in samples stored for several months.



I:	R = H,	$L_2 = (Ph_2P)_2CH_2$
II:	R = H,	$L_2 = (Ph_2As)_2CH_2$
III:	R = H,	$L_2 = Me_4P_2$
IV:	R = H,	$L_2 = (Me_2P)_2CH_2$
V:	R = H,	$L_2 = (F_2P)_2NMe$
VI:	R = H,	$L_2 = [(MeO)_2P]_2NMe$
VII:	R = H,	$L_2 = [(CF_3CH_2O)_2P]_2CH_2$
VIII:	R = Me,	$L_2 = (Ph_2P)_2CH_2$



IX: $L_2 = (Ph_2P)_2CH_2$

Carbonyl stretching frequencies of the various biphenylbis(chromiumdicarbonyl) compounds decrease in the order: $CO > (F_2P)_2NCH_3 > [(CF_3CH_2O)_2P]_2CH_2 > [(CH_3O)_2P]_2NCH_3 > [(C_6H_5)_2As]_2CH_2 > (CH_3)_4P_2 > [(C_6H_5)_2P]_2CH_2 > [(CH_3)_2P]_2CH_2$ which parallels the expected order of increasing electron donation by the ligands. A similar trend is observed for the mononuclear compounds, $C_6H_6Cr(CO)_2L$, for which the carbonyl stretching frequencies decrease in the order [9] : $CO > (CF_3CH_2O)_3P > (CH_3O)_3P > (C_6H_5)_3As > (C_6H_5)_3P > (CH_3)_3P$.

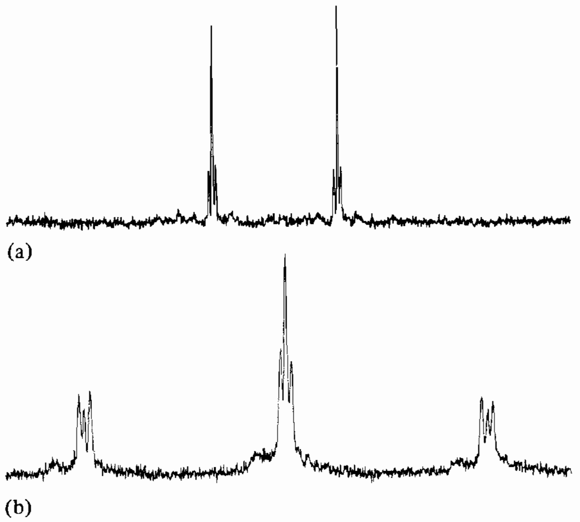


Fig. 1. (a) ^{19}F NMR spectrum of V; (b) ^{31}P NMR spectrum of V.

^1H, ^{19}F and ^{31}P NMR spectra of these compounds have been obtained. With the exception of the μ-$(F_2P_2)_2NCH_3$ complex (**V**) the ^{31}P resonances of the biphenyl$[Cr(CO)_2]_2$-μ-diphosphine compounds were found to be sharp singlets, while the analogous resonance of the dppm manganese complex (**IX**) was broadened due to coupling with the 5/2 spin manganese nucleus. The ^{19}F and ^{31}P spectra of the $(F_2P)_2NMe$ bridged complex, Fig. 1, appear as a complex, second order pattern. In addition, the ^{31}P NMR spectrum of this compound contains a smaller, less well-resolved set of resonances which are offset slightly downfield from the main set. These resonances do not appear to be related to features of the second order spectrum and do not disappear even after rigorous purification of the compound. We believe that this second set of resonances is due to a second conformer of the product which is in equilibrium with the primary conformer in solution. This conformer probably arises from twisting of the ligand or a Walden inversion of the amine methyl group. There was no evidence for a second conformer in the ^{31}P NMR spectrum of **VI**.

The ^{31}P NMR spectrum of **VIII** consists of an AB quartet. In a recent study of a series of $RC_6H_5Cr(CO)_2P(C_6H_5)_3$ compounds we have established that ^{31}P chemical shifts are sensitive to ring substitution with electron donating ring substituents shifting the resonance to lower field [10]. By analogy, it seems likely that the downfield resonance of the AB quartet of **VIII** can be assigned to the methyl substituted phenyl ring while the upfield resonance is assigned to the unsubstituted phenyl ring.

Mass spectra of several of these compounds were obtained and in all cases yielded a parent mass and a fragmentation pattern in which carbonyl ligands are sequentially lost by the fragmenting ions.

TABLE 1. Summary of dihydrogen evolution studies

Compound	Acid[a]	Time (min)	Reaction (%)	H_2	HD	D_2
I	A	20	65	4	15	81
I	A	3	32	28	16	56
II	A			13	25	62
IV	A	3	54	3	14	83
IV	B	10	100	100		
IV	C	720	9	100		
III	A	10	10	8	31	61
V	A	150	3		trace	trace

[a] A = DBF_3OD, B = HCF_3SO_3, C = HCF_3CO_2.

Protonation and Dihydrogen Liberation Studies

We have previously reported that **I** and **II** will react with HBF_3OH to yield dihydrogen and a blue reaction solution from which only fragments of **I** and **II** can be isolated [6]. We have now extended these studies to four additional dinuclear chromium compounds as well as to the manganese compound (**IX**).

Dihydrogen liberation studies were carried out using a high vacuum line outfitted with a Toeppler pump, gas measuring volume and sampling tube. A swivel side-arm on the reaction flask permitted the acid to be degassed prior to its reaction with the metal complex. In a typical reaction, the swivel side-arm was charged with acid and a sample of metal complex was placed in the reaction flask along with a teflon coated spin bar. The apparatus was mounted on the vacuum line and the acid frozen prior to evacuating the reaction flask. The acid was degassed by three freeze–pump–thaw cycles and allowed to come to room temperature (about 27 °C) before being poured onto the metal complex. After several minutes, the reaction mixture was frozen and the non-condensible gases were pumped by the Toeppler pump into the gas measuring and sampling line. Several acids were used in these studies including DBF_3OD which is prepared by bubbling BF_3 into D_2O.

Table 1 summarizes the results of these studies. Extensive dihydrogen evolution is observed for **I**, **IV** and **VIII** in DBF_3OD with the observed rate of dihydrogen evolution of **IV** being almost twice as fast as that from the dppm bridged compounds. Trifluoromethylsulfonic acid, CF_3SO_3H, also reacts rapidly with **IV**, and even trifluoroacetic acid was found to react with **IV** although the rate of dihydrogen evolution was very slow. **III** reacts with DBF_3OD at about 20% of the rate of **IV** while **V** dissolves in the acid to give a brightly colored red solution but does not yield dihydrogen. Compound **IX** reacts in acid to yield dihydrogen at a low rate. It must be noted that the observed rates should not be considered to be true kinetic measurements since factors such as rate of dissolution, surface area of the solid and sampling efficiency in the Toeppler line are not well controlled.

Attempts to recover the starting materials from the acid reactions by addition of tin(II) chloride followed by extraction with methylene chloride were unsuccessful in all cases. We have previously reported that **I** cannot be recovered from its reactions with acids. In this case, $(\eta^5\text{-}C_6H_5C_6H_5)Cr(CO)_2\text{-}[(C_6H_5)_2P]_2CH_2$ in which only one end of the diphosphine is bound was isolated from reactions of **I**. Similarly, reactions of **IV** gave biphenylchromiumtricarbonyl, but no arene species containing a diphosphine group. Recent electrochemical studies of **I** by Geiger *et al.* have shown that dications of **I** are unstable to disproportionation to give the dangling dppm species previously observed and unidentified chromium byproducts [11]. It is likely that a similar disproportionation reaction is occurring to the dications of the other compounds to give the observed fragments.

In addition to determining the relative rates of reaction for each of the compounds in acids, the relative H_2:HD:D_2 ratios of the product gases were also measured for reactions in which DBF_3OD was the reactant acid. These data are presented in Table 1. In all cases, D_2 was found to be the major, but not exclusive, product with varying amounts of HD and H_2 being observed. We take the ratio of H_2:HD:D_2 to be an indication of the extent of ring (or ligand) hydrogen exchange which occurs prior to dihydrogen liberation. In all of the reactions in the present study, some hydrogen exchange must be occurring prior to, or concurrent with, the steps which lead to dihydrogen liberation. Again, problems with reactant mixing and sampling of the product gases give substantial data scatter from one run to the next.

The overall model which arises from these observations is one in which metal basicity and proximity play a significant role in determining whether a complex will react with acid to liberate dihydrogen. For example, both benzenechromium dicarbonyl triphenylphosphine and cyclopentadienylmanganese dicarbonyl triphenylphosphine are protonated in strong acids to give stable species. In contrast, the electronically similar μ-dppm derivatives react to liberate dihydrogen. For a series of similar dinuclear chromium compounds, **I**, **II**, **IV** and **V**, the relative rate of hydrogen evolution appears to be determined by the electron donating ability of the diphosphine ligand and thus by the basicity of the metal atom.

There is, of course, the possibility that the dihydrogen evolution is driven by the observed disproportionation and decomposition reaction. We believe that the electrochemical studies which have been carried out clearly indicate that it is the dication which is undergoing decomposition, but we cannot rule out a secondary series of reactions which might be responsible for the observed dihydrogen reaction. Furthermore, the dihydrogen liberation reactions of ferrocenes and dinuclear cyclopentadienyl rhodium compounds occur with the formation of stable dications.

We have previously suggested a mechanism for dihydrogen evolution in which sequential protonation of the two metal atoms in a dinuclear complex was followed by interaction of the metal hydrides to liberate dihydrogen and leave an oxidized metal complex [4]. Such a mechanism is generally consistent with the experimental observations [12], but presumes a symmetric interaction between the metal hydrides which is precluded by theory [13]. Since the time of our original work on this problem additional electrochemical and structural evidence has become available which bear on these reactions and suggest modifications of the proposed mechanism which may serve as models for additional work.

Electrochemical studies of the oxidation of **I** by Geiger *et al.* have shown that removal of one electron from **I** produces a stable, charge delocalized monocation [11]. The structures of both **I** and its monocation have been determined. **I** was found to have a structure in which the two phenyl rings are twisted relative to one another apparently to accommodate the steric demands of the dppm bridge. A very similar structure has recently been reported by Herrmann *et al.* [8] for **IX**. The monocation of **I** was found to have undergone a dramatic structural reorganization in which the two phenyl rings are almost coplanar and the metal atoms have moved significantly closer together than they were in the neutral species (4.828(1) Å in the neutral species and 4.374(2) Å in the monocation). This structural rearrangement is reminiscent of the structures of [0.0]ferrocenophane and its monocation in which the metals are closer together in the monocation than they are in the neutral species [14].

Although the explanation for these structural rearrangements upon oxidation is not yet clear, it is apparent that the distance between the metal atoms in these dinuclear complexes reduces upon oxidation. If a similar reorganization occurs upon protonation, then it becomes easier to envision structures in which two metal hydrides can interact, or structures in which the second metal acts either directly or indirectly to donate electron density to the first protonated metal atom. Hillman and his coworkers have demonstrated that structural modifications to [1.1]ferrocenophane which decrease the ability of the metal hydrides to approach one another lower the rates of dihydrogen liberation relative to compounds where the approach is enhanced [12]. This combined evidence suggests that dihydrogen evolution may arise in part because of a structural and/or electronic rearrangement of a monoprotonated species resulting in a species in which the metal atoms are closer together than might be otherwise anticipated.

Experimental

^{1}H, ^{19}F and ^{31}P NMR spectra were recorded on a Varian FT80A spectrometer operating at room temperature. IR spectra were recorded on a Perkin-Elmer 1750 FTIR spectrometer. Electronic spectra were recorded using a Beckman DU-7 spectrophotometer. Electron impact mass spectra were recorded on a Finnigan model 4610 mass spectrometer at the University of Vermont. Gas samples from the dihydrogen evolution studies were analyzed using a CEC Type 21-621 mass spectrometer. A GOW-MAC model 080–20 HPLC using a 25 cm silica gel column and 3:7 THF:petroleum ether as an elutant was used for analysis of reaction mixtures and as a confirmation of sample purity after preparatory columns and recrystallization. Elemental analyses were conducted by Galbraith Laboratory, Inc. of Knoxville, TN and Analytic Microlab, Inc. of Atlanta, GA.

Biphenylbis(chromiumtricarbonyl) [15], $(C_{10}H_8)Mn_2(CO)_4$-μ-dppm [8], Me_4P_2, $(MeO)_2P_2NMe$ [16], dppm and dmpm were prepared by standard literature procedures. The preparation of $(C_{12}H_{10})Cr_2(CO)_4$-μ-dppm and μ-dpam as well as the details of the experimental procedures for examining the reactions of dinuclear compounds and strong acids have been reported previously [6]. UV photolysis reactions were conducted in a water-cooled Ace doubly jacketed photochemical reactor using a medium pressure Hanovia lamp. All reactions were conducted under purified nitrogen using solvents which were dried and distilled under nitrogen.

Synthesis of Bis[di(2,2,2-trifluoroethoxy)-phosphido]methane

Bis(dichlorophosphido)methane, 61.2 g (0.28 mol), pyridine, 90 ml (1.13 mol) and diethyl ether (500 ml) were added to a 2 l, three-necked flask fitted with a mechanical stirrer, Fredrich's condenser and a pressure equalizing dropping funnel. The reaction flask was placed in a dry ice/acetone bath (−78 °C). After the mixture in the flask had cooled to −78 °C, 2,2,2-trifluoroethanol, 112 g (1.12 mol), was added dropwise over a period of 2 h under constant stirring. After the addition was complete the reaction mixture was allowed to come to room temperature and stirred for 1 h. The reaction mixture was then filtered through Celite to remove pyridine hyCorchloride. The contents of the filter were washed with 200 ml of cold diethyl ether. Diethyl ether was removed from the yellowish filtrate in a flash evaporator. The residue was distilled under vacuum. A water white liquid, 28 g, was collected at 24–28 °C (0.02 mm) and was shown by ^{1}H, ^{19}F and ^{31}P NMR to be $P(OCH_2CF_3)_3$. Continued distillation gave the product, $[(CF_3CH_2O)_2P]_2CH_2$, which was collected as a water white liquid at 67–70 °C (0.016 mm), 52 g, 40% yield. All NMRs were recorded in C_6D_6. ^{1}H NMR: 3.66 ppm (8H, septet, J(P–H) = J(F–H) = 4.1 Hz), 1.80 ppm (2H, triplet, J(P–H) = 7.07 Hz). ^{19}F NMR: 87.53 (doublet of triplets). $^{31}P\{^{1}H\}$ NMR: 71.41 ppm (septet, J(P–F) = 3.27 Hz).

Synthesis of 4-Methylbiphenylbis(chromiumtricarbonyl)

$Cr(CO)_6$, 4.4 g (20 mmol), and 4-methylbiphenyl, 1.68 g (10 mmol) were taken up in a mixture of butyl ether with 5% THF and refluxed for 5 days. After filtration of the hot reaction mixture to remove chromium oxide decomposition products, the solvent was removed to give an orange–yellow solid. Extraction with hot heptane removed 0.60 g of 4-methylbiphenyl$Cr(CO)_3$ as a yellow powder, melting point (m.p.) 88–90 °C. Yield: 20%. IR:(CH_2Cl_2) 1966(s), 1890(s). NMR: ($CDCl_3$) 7.40 (m, 5H), 5.78, 5.30 (pseudo AB quartet, J(A–B) = 6.7 Hz, 4H), 2.38 (s, minor component), 2.22 (s, major component). NMR indicates that two isomers are present in which the $Cr(CO)_3$ moiety is present on different arene rings. As expected the species in which the $Cr(CO)_3$ is on the methylated ring is the major component of this mixture. *Anal.* Calc. for $C_{16}H_{12}O_3Cr$: C, 63.16; H, 3.95. Found: C, 62.69; H, 4.07%. The orange solid which remained after heptane extraction was recrystallized from benzene/petroleum ether to give 2.7 g of an orange solid, m.p. 158–160 °C with decomposition. Yield: 61%. IR: (CH_2Cl_2) 1965(s), 1900(s). NMR: ($CDCl_3$) 5.76–5.20 (m, 9H), 2.22 (s, 3H). *Anal.* Calc. for $C_{19}H_{12}O_6Cr_2$: C, 51.82; H, 2.73. Found: C, 52.09; H, 2.79%.

General Procedure for Synthesis of μ-Diphosphine Derivatives

Biphenylbis(chromiumtricarbonyl), 1.0 g (2.35 mmol) and an equivalent quantity of diphosphine were placed in an Ace double-jacketed photolysis apparatus which had been flushed with nitrogen for 30 min. Freshly distilled benzene, about 240 ml, was added to the reaction vessel. (In cases where the diphosphine was air sensitive, it was transferred by syringe after the solvent was added to the reaction vessel.) A steady stream of purified nitrogen was passed through the reaction solution. The mixture was photolyzed overnight during which time a deep red color developed. The reaction mixture was transferred to a nitrogen flushed round bottom flask by cannuli and most of the solvent removed by rotary evaporator. When 5–10 ml of solvent remained, petroleum ether was added to the concentrate and the resulting precipitate collected. This precipitate could be purified by column chromatography using alumina and mixtures of dichloromethane and petroleum ether as an elutant. Alternatively, several compounds could be purified directly by recrystallization from benzene/petroleum ether. New compounds prepared by this procedure include the following:

$C_{12}H_{10}[Cr(CO)_2]_2$-μ-Me_4P_2

IR: (CH_2Cl_2) 1886(s), 1831(s). UV–Vis: (CH_2Cl_2) 317 (13760), 425 (3270). ^{1}H NMR: ($CDCl_3$) 4.69 (t, 2H), 4.23 (t, 4H), 3.88 (m, 4H), 1.21 (s, 12H). ^{31}P NMR: ($CDCl_3$) 68.88(s). MS: 492 (M^+), 436 (M^+–2CO), 408 (M^+–3CO), 380 (M^+–4CO). *Anal.* Calc. for $C_{20}H_{22}O_4P_2Cr_2$: C, 48.79; H, 4.50; P, 12.58. Found: C, 49.29; H, 4.91; P, 12.65%. m.p. 194–195 °C dec. Yield: 36.3%.

$C_{12}H_{10}[Cr(CO)_2]_2$-μ-$[(Me_2)_2P]_2CH_2$ (IV)

IR: (CH_2Cl_2) 1880(s), 1820(s). ^{1}H NMR: ($CDCl_3$) 5.08 (m, 4H), 4.70 (t, 4H), 4.05 (t, 2H), 1.85 (t, J(P–H) = 9.8 Hz, 2H), 1.20 (d, J(P–H) = 6.2 Hz, 12H). ^{31}P NMR: ($CDCl_3$) 45.67(s). UV–Vis: (CH_2Cl_2) 334 (12450), 430 (1900). MS: 506 (M^+), 450 (M^+–2CO), 422 (M^+–3CO), 394 (M^+–4CO). *Anal.* Calc. for $C_{21}H_{24}P_2O_4Cr_2$: C, 49.80; H, 4.74; P, 12.25. Found: C, 49.94; H, 5.01; P, 11.74%. Orange crystals, m.p. 221–223 °C, dec. Yield 8.4%.

$C_{12}H_{10}[Cr(CO)_2]_2$-μ-$(F_2P)_2NMe$ (V)

IR: (CH_2Cl_2) 1928(s), 1878(s). UV–Vis: (CH_2Cl_2) 322 (12032), 410 (2106). ^{1}H NMR: (C_6D_6) 4.80 (broad s, 4H), 4.34 (broad s, 6H), 2.81 (broad t, J(P–H) = 5.73 Hz, 3H). ^{19}F NMR: (C_6D_6, $CFCl_3$ ref.) 10.6 ppm (^{1}J(P–F) = 1177 Hz, ^{4}J(P–F) = 6.9 Hz, ^{5}J(F–F) = 32.7 Hz). ^{31}P NMR: (C_6D_6) 149.5 ppm (^{2}J(P–P) = 30 Hz). MS: 537 (M^+), 509 (M^+–CO), 481 (M^+–2CO), 453 (M^+–3CO), 425 (M^+–4CO). *Anal.* Calc. for $C_{17}H_{13}O_4Cr_2NP_2F_4$: C, 37.99; H, 2.42; P, 11.74. Found: C, 39.06; H, 2.85; P, 11.74%. m.p. 160 °C dec. Yield: 65%.

$C_{12}H_{10}[Cr(CO)_2]_2$-μ-$[(MeO)_2P]_2NMe$ (VI)

IR: (CH_2Cl_2) 1894(s), 1850(s). ^{1}H NMR: ($CDCl_3$) 5.16 (broad t, 6H), 4.95 (broad d, 4H), 3.57 (d,

J(P–H) = 11.68 Hz, 12H), 2.89 (t, J(P–H) = 7.79 Hz, 3H). $^{31}P\{^1H\}$ NMR: ($CDCl_3$) 211.17(s). *Anal.* Calc. for $C_{21}H_{25}O_8Cr_2P_2N$: C, 43.07; H, 4.27; N, 2.39; P, 10.60. Found: C, 43.15; H, 4.35; N, 2.34; P, 10.60%. Yellow solid, m.p. 188 °C dec. Yield: 33%.

$C_{12}H_{10}[Cr(CO)_2]_2$-μ-$[(CF_3CH_2O)_2P]_2CH_2$ *(VII)*

IR: (CH_2Cl_2) 1910(s), 1867(s). ^1H NMR: ($CDCl_3$) 5.43–5.02 (m, 10H), 4.20 (broad m, 8H), 3.06 (t, J(P–H) = 8 Hz, 2H). ^{19}F NMR: ($CDCl_3$, C_6F_6 ref.) 87.38 (t, J(F–H) = 7.04 Hz). ^{31}P NMR: ($CDCl_3$) 214.03(s). Orange needles, m.p. 167–168 °C. Yield: 7.2%. Insufficient quantities of this compound were available for analysis.

$CH_3C_{12}H_9[Cr(CO)_2]_2$-$\mu$-dppm *(VIII)*

IR: (CH_2Cl_3) 1880(s), 1823(s). ^1H NMR: ($CDCl_3$) ^{31}P NMR: ($CDCl_3$) 77.36, 75.61 (AB quartet, J(A–B) = 23.0 Hz). *Anal.* Calc. for $C_{21}H_{24}O_4P_2Cr_2$: C, 49.80; H, 4.74. Found: C, 49.87; H, 4.78%. Orange crystals, m.p. 214–216 °C, dec. Yield: 34%.

Acknowledgements

T.E.B. wishes to thank the Research Corporation for their support of this research. We thank Professor William Geiger of the University of Vermont for obtaining the mass spectra of the diphosphine compounds described in this report. We thank Professor R. Bruce King of the University of Georgia for making available details of the preparations of several diphosphines prior to their publication, and for his helpful suggestions on the syntheses.

References

1 (a) R. C. Brady and R. Pettit, *J. Am. Chem. Soc., 102* (1980) 1681; (b) *103* (1981) 1287; (c) R. Poliblanc, *Inorg. Chim. Acta, 62* (1982) 75.

2 J. E. Sheats, R. S. Czernuszewicz, G. C. Dismukes, A. L. Rheingold, V. Petrouleas, J. Stubbe, W. H. Armstrong, R. H. Beer and S. J. Lippard, *J. Am. Chem. Soc., 109* (1987) 1435, and refs. therein.

3 U. T. Muller-Westerhoff and A. I. Nazzal, *J. Am. Chem. Soc., 106* (1984) 5381.

4 T. E. Bitterwolf and A. C. Ling, *J. Organomet. Chem., 57* (1973) C15.

5 T. E. Bitterwolf, W. C. Spink and M. D. Rausch, *J. Organomet. Chem., 363* (1989) 189.

6 T. E. Bitterwolf, *J. Organomet. Chem., 252* (1983) 305.

7 (a) B. V. Lokshin, A. G. Ginzburg, V. N. Setkina, D. N. Kursanov and I. B. Nemirovskaya, *J. Organomet. Chem., 37* (1972) 347; (b) A. G. Ginzburg, P. O. Okulcvich, V. N. Setkina, G. A. Panosyan and D. N. Kursanov, *J. Organomet. Chem., 81* (1974) 201; (c) A. C. Ginzburg, P. V. Petrovskii, V. N. Setkina and D. N. Kursanov, *Izvest. Akad. Nauk SSSR, Ser. Khim.,* (1985) 186.

8 W. A. Herrmann, D. Andrejewski and E. Herdtweck, *J. Organomet. Chem., 319* (1987) 183.

9 T. E. Bitterwolf, *Polyhedron, 2* (1983) 675; (b) *5* (1988) 409.

10 T. E. Bitterwolf, *Polyhedron, 7* (1988) 1377.

11 N. Van Order, Jr., W. E. Geiger, T. E. Bitterwolf and A. L. Rheingold, *J. Am. Chem. Soc., 109* (1987) 5680.

12 M. Hillman, S. Michaile, S. W. Feldberg and J. J. Eisch, *Organometallics, 4* (1985) 1258.

13 (a) G. Trinquier and R. Hoffman, *Organometallics, 3* (1984) 370; (b) A. Sevin, Y. Hengtai and P. Chaquin, *J. Organomet. Chem., 262* (1984) 391; (c) A. Waleh, G. H. Loew and U. T. Muller-Westerhoff, *Inorg. Chem., 23* (1984) 2859.

14 M. Hillman and A. Kvick, *Organometallics, 2* (1983) 1780.

15 S. Top and G. Jaouen, *J. Organomet. Chem., 182* (1979) 184.

16 G. M. Brown, J. E. Finhold, R. B. King and J. W. Bibber, *Inorg. Chem., 21* (1982) 2139.