Journal of Organometallic Chemistry, 91 (1975) 87—95

ORGANOMETALLIC LIGANDS

III*. THE ELECTROCHEMISTRY OF FERROCENYLPHOSPHINES AND THEIR COMPLEXES

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(Received July 16th, 1974)

Summary

The electrochemistry of the ferrocenylphosphines $FcPh_2P$, Fc_2PhP and Fc_3P (where Fc is the monosubstituted ferrocenyl group) and their complexes of the type $L \cdot BH_3$, LMe^+I^-, $LM(CO)_5$ and $L_2M(CO)_4$ (M = Mo, W) has been examined by cyclic voltammetry in CH_2Cl_2. Well-defined, one-electron, reversible redox waves were observed for the oxidation of each ferrocenyl group (in the range $E_{\text{peak, anodic}}$ = +0.65 to +1.10 V vs. SCE), except for Fc_3P and its complexes where the redox waves overlapped. Upon complexation, $E_{\text{peak, anodic}}$ for ferrocenyl group oxidation increased (by +0.15 to +0.39 V) for $FcPh_2P$ complexes; however, essentially no change was observed for the complexes of Fc_2PhP or Fc_3P, except for their phosphonium salts, LMe^+I^-. $E_{\text{peak, anodic}}$ of the metal in the hexacarbonyls, $M(CO)_6$, was lowered to an experimentally accessible potential by replacement of a CO ligand or ligands by the poorer π-acceptor ligand, the phosphine. However, the metal was still oxidized (irreversibly) at potentials somewhat higher than the ferrocenyl groups ($E_{\text{peak, anodic}}$ = +1.16 to +2.05 V vs. SCE). In the series of complexes from $(Ph_3P)W(CO)_5$ to $(Fc_3P)W(CO)_5$ there is a general increase in tungsten $E_{\text{peak, anodic}}$, the increase apparently resulting from an increasing number of ferrocenyl groups being oxidized before the tungsten oxidation step. Infrared spectra of the solutions of metal carbonyl complexes of the type $LM(CO)_5$ at various stages of ferrocenyl group oxidation showed that the intense $E/A_1{}^1$ mode shifted to higher frequencies by about 5 cm^{-1} for each ferrocenyl group oxidized. This suggests that the coordinating ability of the ferrocenylphosphines is not appreciably altered upon oxidation.

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* See refs. 1 and 2 for parts I and II.

Introduction

Our current research interests concern organometallic ligands, and we have recently been investigating those based on ferrocene [1,2]. Such ligands are expected to be electroactive and, because of this, may enable us to prepare coordination complexes having unusual chemical and physical properties. For example, McCleverty and his co-workers have recently reported that the cyclic voltammogram for the oxidation of $Cr(CO)_5[FcC(X)]$ (where Fc is the monosubstituted ferrocenyl group and X is OEt, OMe, or pyrrolidin-1-yl) does not show the expected two separate oxidation steps (one each for $Cr^0 \rightarrow Cr^+$ and $Fe^{2+} \rightarrow Fe^{3+}$) or a single, two electron step [3]. Rather, only one electron is removed, an observation which was explained by stating that "the redox orbital of the $Cr(CO)_5$-$[FcC(X)]$ complex encompasses both potential redox centers (and the single redox wave) corresponding to the generation of $[A—B]^+$".

Another reason for examining the electrochemical behavior of multi-metal compounds is the possibility of generating mixed valence compounds which exhibit intervalent electron transfer [4]. Several examples of such compounds containing several ferrocene moieties have been reported recently [5,6].

In anticipation of turning our attention toward the preparation of ferrocene-containing mixed valence compounds and to an examination of the influence of oxidized ligands on reactions at coordinated metal centers, we have systematically examined the electrochemistry of the previously reported ferrocenylphosphines $FcPh_2P$, Fc_2PhP, and Fc_3P, and their coordination complexes [1]. Our purpose was to detect any change in coordinating ability of the organometallic ligand upon oxidation, and any changes in the potential for oxidation of the ferrocenyl group or coordinated metal as the central metal or ligand, respectively, are changed*.

Experimental

Electrochemical techniques

All electrochemical experiments were done on a multipurpose electroanalytical instrument designed by Woodward and Ridgway [8]. The working electrode and auxiliary electrode were a 3 mm length of platinum wire and a platinum wire spiral, respectively. The reference electrode was saturated calomel (SCE).

Cyclic voltammetry experiments were done on 2 mM solutions in reagent grade dichloromethane with 0.2 M tetra-n-butylammonium perchlorate (TBAP) (G.F. Smith Co.) as a supporting electrolyte. Solutions were degassed with dry nitrogen before each experiment, and a nitrogen blanket was kept over the solutions at all times. Sweep rates varied from 1 to 0.1 V/s over a range of +2.5 to —1.5 V. E_{peak} values are listed in Table 1.

For all controlled potential coulometry experiments, a current—voltage booster amplifier was utilized so that larger currents could be handled. The working electrode was a platinum gauze basket referenced against SCE.

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* For a review of organometallic electrochemistry, see ref. 7. (This review is particularly pertinent to the results reported here.)

Results of the coulometry experiments are also listed in Table 2. It should be noted that some difficulty was experienced in determining accurately the number of electrons involved in oxidations of Fc_3P and its complexes. This difficulty, apparently due to adsorption of the electroactive compound at the electrode, was examined in a thorough study of the coulometry of $(Fc_3P)W(CO)_5$. A known amount of the compound was first oxidized at +0.70 V until the current approached zero; the number of electrons consumed per mole of the compound was found to be 0.8 instead of the expected 1.0. Therefore, the same amount of compound was added to the solution containing the already oxidized $(Fc_3P)W(CO)_5$; upon oxidation again at +0.70 V, the electron count for the added material was 1.07. A possible explanation for this result is that, when the compound was first added to the solution, some of it was adsorbed onto the platinum electrode and altered irreversibly so that it was no longer electroactive; only that remaining in solution could be oxidized. When the second sample was added, all of the "active" electrode adsorption sites had been filled so the entire amount of added material was available for oxidation.

Infrared spectra of solutions of the metal carbonyl complexes were done before and after electrolysis in a demountable cell with a 0.1 mm path length and NaCl windows on a Perkin—Elmer 257. All oxidized species were stable in air for short periods of time, and a sample could be transferred by syringe from the electrochemical cell into the infrared cell without adverse effect.

Preparation of $L_2M(CO)_4$

The preparation and characterization of the compounds used in this electrochemical survey, with the exception of those of the type $L_2M(CO)_4$, have been described previously [1]. The disubstituted metal carbonyl derivatives, $L_2M(CO)_4$ (where L = $FcPh_2P$ or Fc_2PhP and M = Mo or W), were prepared by the method of Chatt and co-workers [9]. The phosphine (2 mmol) and $NaBH_4$ (2 mmol) were refluxed with the appropriate metal hexacarbonyl (1 mmol) in a 1/1 mixture of tetrahydrofuran and ethanol. (It might be noted that one of the advantages of this procedure is that it is not necessary to perform the reaction under an inert atmosphere.) A reflux time of 5 h was needed for $(FcPh_2P)_2Mo(CO)_4$, while $(Fc_2PhP)_2W(CO)_4$ required an overnight reflux. Following the reflux period, the solutions were allowed to cool and were stirred for several hours to aid precipitation. The solvent was partially evaporated, and the remaining solution was filtered. The resulting yellow-orange precipitates were recrystallized from dichloromethane/petroleum ether.

Physical and analytical data are as follows:

$(FcPh_2P)_2Mo(CO)_4$: m.p. 219-222°C. $\nu(CO)$ (cm^{-1}) 1925 w, 1870 vs. Analysis found: C, 60.61; H, 4.13. Calcd.: C, 60,76; H, 4.01%.

$(Fc_2PhP)_2W(CO)_4$: m.p. 300°C. $\nu(CO)$ (cm^{-1}) 1850 vs. Analysis found: C, 53.52; H, 3.73. Calcd.: C, 53.67; H, 3.67%.

Results

The electrochemical results are compiled in Tables 1 and 2*. It should be noted first that all of the ferrocenyl group oxidations are apparently electro-

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* See part I (ref. 1) for the figures of the cyclic voltammograms for $FcPh_2P$ and $(FcPh_2P)Mo(CO)_5$.

TABLE 1

CYCLIC VOLTAMMETRY DATA FOR THE FERROCENYLPHOSPHINES AND THEIR COMPLEXES[a]

Compound	Ferrocenyl group redox waves E_{peak} (V vs. SCE)		Coordinated metal redox waves E_{peak} (V vs. SCE)
	Anodic	Cathodic	
Ferrocene	+0.59	+0.43	
$FcPh_2P$	+0.72	+0.41	
Fc_2PhP	+0.75	+0.62	
	+0.91	+0.79	
Fc_3P	+0.70	+0.59	
	+0.84		
	+0.91	+0.72[b]	
$FcPh_2PBH_3$	+0.82	+0.70	
Fc_2PhPBH_3	+0.75	+0.62	
	+0.93	+0.80	
Fc_3PBH_3	+0.72	+0.59	
	+0.87		
	+0.93	+0.74	
$FcPh_2PMe^+I^-$ [c]	+1.06	+0.96	
$Fc_2PhPMe^+I^-$	+0.96	+0.86[d]	
	+1.06		
$Fc_3PMe^+I^-$	+0.93	+0.82	
	+1.07	ca. +0.92[e]	
$(Ph_3P)W(CO)_5$			+1.48
$(FcPh_2P)W(CO)_5$	+0.82	+0.70	+1.54
$(Fc_2PhP)W(CO)_5$	+0.78	+0.64	+1.52
	+0.96	+0.83	
$(Fc_3P)W(CO)_5$	+0.70	+0.58	+1.92
	+0.87	+0.77	
	+0.96	+0.84	
$(FcPh_2P)Mo(CO)_5$	+0.82	+0.65	+1.56
$(Fc_2PhP)Mo(CO)_5$	+0.69	+0.49	+1.35
	+0.88	+0.68	
$(Fc_3P)Mo(CO)_5$	+0.68	+0.54	+2.05
	+0.86	+0.72[f]	
	+0.92	+0.76	
$(FcPh_2P)_2Mo(CO)_4$	+0.72	+0.55	+1.16
$(Fc_2PhP)_2W(CO)_4$	+0.76	+0.53	+1.32
	+0.91	+0.69	

[a] All data obtained from 2 mmolar solutions of compound in CH_2Cl_2: 0.2 M Bu_4NClO_4 used as supporting electrolyte. [b] See Discussion. [c] Poorly defined waves were observed at about +0.4 and +0.7 V for all of the MeI complexes. These waves are presumably due to the presence of I^- [16]. [d] Reduction apparently occurs as a simultaneous addition of two electrons. Same behavior as Fc_3P and its complexes. [e] The second redox wave is presumably a two electron oxidation and reduction. [f] The second and third cathodic waves are very close and their position is estimated.

chemically reversible according to the following criteria:

(a). The amount of current flowing on oxidation and reduction was the same or nearly so.

(b). According to controlled potential coulometry experiments, the same number of electrons was lost on oxidation as was gained in re-reduction.

(c). The theoretical difference in peak potentials for anodic and cathodic

TABLE 2

CONTROLLED POTENTIAL COULOMETRY DATA FOR THE FERROCENYLPHOSPHINES AND SOME COMPLEXES[a]

Compound	Oxidizing potential (V vs. SCE)	No. of electrons n
$FcPh_2P$	+0.80	1.15
Fc_2PhP	+0.75	1.05
	+1.10	1.13
Fc_3P	+0.72	1.03
	+1.00	1.40[b]
$(FcPh_2P)Mo(CO)_5$	+0.90	1.06
$(Fc_2PhP)Mo(CO)_5$	+0.70	1.00
	+1.00	1.06
$(Fc_3P)MO(CO)_5$	+0.70	0.89[b]
	+1.00	1.34[b]
$(FcPh_2P)W(CO)_5$	+0.90	0.98
$(Fc_2PhP)W(CO)_5$	+0.76	1.02
	+1.05	1.08
$(Fc_3P)W(CO)_5$	+0.70	0.80-1.03[b]
	+1.00	1.40-1.63[b]
$(FcPh_2P)_2Mo(CO)_4$	+0.80	1.95
$(FcPhP)_2W(CO)_4$	+1.00	ca. 3.8[b]

[a] All data obtained using 2 mmolar solutions of compound in CH_2Cl_2; 0.2 M Bu_4NClO_4 used as supporting electrolyte. [b] Electrode adsorption interferred. See Experimental section.

cyclic voltammetric waves is 56 mV for a reversible process. However, solvents and cell design can affect this difference in practice. For example, McCleverty and his co-workers [3] have reported peak separations of 170 to 230 mV for reversible oxidations of complexes of the type $Cr(CO)_5L$ (where L is a variety of phosphines and amines) in CH_2Cl_2, the same solvent used herein. Moreover, we have observed a separation of 130 mV for ferrocene (2 mM in CH_2Cl_2 with 0.2 M tetra-n-butylammonium perchlorate supporting electrolyte), a system known to be completely reversible at a solid electrode [6,7]. As seen in Table 1, the observed peak separations are well within a range characteristic of a reversible system under these conditions.

(d). Finally, infrared spectra of solutions of $LM(CO)_5$ were examined in some cases after controlled potential oxidation and re-reduction. These spectra were identical with those of the pure complexes.

The number of electrons involved in each step assigned to a ferrocenyl group oxidation is within experimental error of the one electron anticipated (Table 2). However, in the case of the triferrocenylphosphines, electrode adsorption interfered, and the number of electrons passed was less than one per ferrocenyl group. Corrected n values were obtained using a procedure described in the Experimental.

Finally, it should be noted that all of the solutions tested were bright yellow-orange before oxidation. Following oxidation in the controlled potential coulometry experiments, the color changed to blue-green, indicating the presence of ferricenium ions.

Discussion

The ferrocenylphosphines and their complexes of the type $LM(CO)_5$, $L \cdot BH_3$, and LMe^+I^- are electrochemically well-behaved. With a few exceptions*, separate, reversible one-electron redox waves are observed for each ferrocenyl group oxidation. This is in direct contrast with *B*-triferrocenylborazine where all three ferrocenyl iron atoms are oxidized simultaneously at the same potential [10]. However, the ferrocenyl groups are separated by two atoms in the borazine, whereas they are separated by only one in the phosphines. Several investigators have found that the difference between potentials for oxidation of two ferrocenyl groups in the same molecule is markedly dependent on the number of atoms separating the electroactive groups [6,11]. These results suggest that the electrostatic field of the ferricenium ion formed in the first oxidation step is largely responsible for determining the oxidation potential of the second ferrocenyl group when the electroactive groups are separated by no more than one atom.

Several groups have found that the oxidation potential of the ferrocenyl group is "exceptionally sensitive to a small difference in the electronic effects of substituents" [7,12]. For example, ΔE ($E_{1/2}$ for substituted ferrocene $-$ $E_{1/2}$ for ferrocene) is +0.139 V for $FcCONH_2$, +0.120 V for $FcCONHCH_3$, and +0.266 V for $FcCOOCH_3$. It is not surprising, therefore, that the ferrocenyl group oxidation potential increases upon complexation of ferrocenyldiphenylphosphine with BH_3 (ΔE = +0.15 V), $M(CO)_5$ (M = Mo,W) (ΔE = +0.17 V), and MeI (ΔE = +0.39 V). The first two changes in potential are certainly within the range expected, but the last is quite large, apparently because we are oxidizing a species ($FcPh_2PMe^+$) which already bears a positive charge.

Somewhat surprisingly, there is little or no change in the oxidation potential of the ferrocenyl groups upon formation of complexes of Fc_2PhP and Fc_3P, except for the methyl iodide salts. Even in the latter complexes the change in $E_{\text{peak, anodic}}$ is smaller (ΔE = +0.23 V for the first oxidation step) than it was for $FcPh_2PMe^+I^-$ (ΔE = +0.39 V)**. This suggests that, with the attach-

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[*] The cyclic voltammetric behavior of triferrocenylphosphine in dichloromethane is unusual. The first iron atom is oxidized at about the same potential as the first iron atom in $FcPh_2P$ or Fc_2PhP. However, the second step occurs at a lower potential than the second in Fc_2PhP and the third at a considerably lower potential than might have been expected. Furthermore, while the second and third oxidation waves are visibly separated, the first and second re-reduction steps (eqn. 1) apparently occur at the same potential. Similar behavior was observed for the complexes of this ligand as well, although the second and third waves were separated to a slightly greater

$$Fc_3P^{3+} + 2e^- \rightarrow Fc_3P^+ \tag{1}$$

extent. As noted in the Experimental, severe electrode adsorption occurred with triferrocenylphosphine and its complexes and interfered with the controlled potential coulometry experiments. This same adsoprtion is undoubtedly responsible for the unusual cathodic wave form observed in the cyclic voltammetry experiments. Further evidence supporting this point of view is that all three anodic and cathodic waves were to be clearly separated in acetonitrile.

[**] It is interesting to consider the possibility that the potential shift observed for $FcPh_2PMe^+I^-$ (+0.39 V) may be divided into two parts: +0.23 V due to the positive charge on the complex and +0.16 V due to a substituent effect. +0.23 V is of course just the shift observed for the MeI complexes of Fc_2PhP and Fc_3P, and +0.16 V is the average substituent shift observed for the other complexes of $FcPh_2P$.

ment of the second and third electron-donating ferrocenyl groups, there is relatively little change in the net electron density at the iron after complexation to most Lewis acids.

The behavior of the disubstituted metal carbonyl complexes, $(FcPh_2P)_2Mo(CO)_4$ and $(Fc_2PhP)_2W(CO)_4$, is interesting in that the ligands are apparently electrochemically isolated by the intervening metal atom; their electrochemistry closely resembles that of the monosubstituted complexes of the type $LM(CO)_5$*. However, the difference in the ferrocenyl group peak potential for oxidation ($E_{p,a}$'s) between the free ligand and $(FcPh_2P)_2Mo(CO)_4$ is considerably less (ΔE = +0.05 V) than in the case of the monosubstituted analogue (ΔE = +0.17 V). Apparently the replacement of a second carbonyl group by a less capable π-acceptor, the ferrocenylphosphine, means that the extent to which the phosphine donates to the metal is decreased.

Predicting the relative potentials for oxidation of the complexed metals in ferrocenylphosphinemetal carbonyl complexes is not as straightforward as it may seem at the outset. There are several factors to be taken into account: the nature of the metal, the ligand σ-basicity and π-acidity, and the number of carbonyl groups. Intuitively the most reasonable assumption to make is that the electron removed in the oxidation is in the highest occupied molecular orbital and that the relative energy of this molecular orbital is affected in a reasonably predictable manner by the σ-basicity and π-acidity of the ligand [3]. However, this assumption may be true only in a very general sense. McCleverty and his co-workers have found that the replacement of a carbonyl group in $Cr(CO)_6$ by a poorer π-acceptor (a phosphine or an amine) moved the potential for oxidation of the chromium into an experimentally accessible potential region (anodic potentials up to about +2.5 V vs. SCE) [3]. Furthermore, they found a rough correlation between the π-acceptor/σ-donor ratio of the ligand and the potential for metal oxidation: that is, phosphine complexes oxidized at lower potentials than $Cr(CO)_6$ and amine complexes lower still. In addition, replacement of one more carbonyl group to give $(L\text{—}L)Cr(CO)_4$ (L—L = bidentate amines or phosphines) lowered the metal oxidation potential still more. Finally, in a complex more closely related to those reported in this paper, we have found that, when two carbonyl groups of $Cr(CO)_6$ are replaced by PPh_2 and NMe_2 groups of the bidentate organometallic ligand 1-dimethylaminomethyl-2-diphenylphosphinoferrocene, the coordinated chromium is oxidized at a potential less than that of the ligand ferrocenyl group [2].

While the results cited above seem intuitively reasonable, molecular orbital calculations have shown that the highest occupied molecular orbital and the next most tightly bound orbital in complexes of the type $Cr(CO)_5L$ are composed almost exclusively of Cr 3*d*, C 2*p*, and O 2*s* atomic orbital contributions; that is, L does not apparently participate to any significant extent in the orbital assumed to be the redox orbital [3]. Consequently, it is not entirely clear just

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* It should be noted that the observation of a single carbonyl stretching mode for these compounds indicates that the ligands are *trans* (see Experimental). It is by no means certain that the electrochemistry of the *cis* isomer would be the same. Unfortunately, we could find no evidence for the *cis* isomer in the products from the preparation of the disubstituted complexes so that this possibility could be tested.

how L influences the potential for oxidation of the coordinated metal, only that it often does in a seemingly reasonable way. However, given our current lack of theoretical understanding, it is not surprising that predictions are not always borne out in a series of closely related complexes. For example, although McCleverty observed that complexes of phosphites had more positive $E_{1/2}$'s for oxidation than those of phosphines, as might be predicted, $E_{1/2}$ of the metal in $(Me_3P)Cr(CO)_5$ is greater than that in $(Ph_3P)CR(CO)_5$, contrary to expectation [3][*].

Another factor complicating the analysis of trends in metal oxidation potentials for the ferrocenylphosphinemetal carbonyls is that, if the ligand ferrocenyl groups are oxidized before the central metal (as is actually the case), the effect of the electrostatic field of the ferricenium ions would be to elevate the potential for metal oxidation.

In previously published work, we concluded that the coordinating ability of the ferrocenylphosphines increased in the order $Ph_3P < FcPh_2P < Fc_2PhP < Fc_3P$; however, we noted that steric effects frequently decreased the kinetic stability of their complexes [1]. Therefore, on the basis of this work and the foregoing discussion, we might predict that

(i). The coordinated metal will be oxidized at a potential greater than the ligand ferrocenyl groups.

(ii). Increasing basicity with increasing ferrocenyl group substitution would cause the metal in the Fc_3P complexes to be oxidized at the lowest potential in the series.

(iii). Prior oxidation of ferrocenyl groups will offset effects of increasing ligand basicity.

In reality, it would appear that all three effects are operative, thereby producing a non-linear result. The potential for metal oxidation shows a general increase in the series $(Ph_3P)W(CO)_5$ . . . $(Fc_3P)W(CO)_5$, implying that (iii) is chiefly responsible for the observed effect[**]. However, the potential for the oxidation of the coordinated metal in $(Fc_2PhP)M(CO)_5$ is slightly smaller than the corresponding value for $(FcPh_2P)M(CO)_5$.

The effect of replacing a carbonyl group with a poorer π-acceptor ligand is also apparent in the oxidation of the central metal in the two disubstituted complexes. In both cases the metal oxidizes at a very low potential compared with $(Ph_3P)W(CO)_5$, for example, even in spite of the fact that two or four ferrocenyl groups have been oxidized prior to oxidation of the coordinated metal.

Finally, with regard to oxidation of the coordinated metal, the molybdenum and tungsten oxidations were all irreversible. This is in direct contrast to the reversible oxidation of chromium in similar complexes and in $(FcCNP)Cr(CO)_4$ (FcCNP = 1-dimethylaminomethyl-2-diphenylphosphinoferrocene) [2,3].

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[*] The pK values of Henderson and Streuli and Tolman's substituent parameters both predict a greater coordinating ability for tertiary phosphines than for phosphites; they also predict that Me_3P should be more basic than Ph_3P [13,14].

[**] Yet another explanation for the observed trend is that, as the phosphine becomes increasingly bulky with added ferrocenyl groups, the equilibrium P—M bond distance increases, thereby decreasing the effective basicity of the ligand. The net result would be a decrease in the ligand field strength of the ligand and an increase in the binding energy of the redox orbital.

The effect of ligand oxidation was also examined by observing changes in the carbonyl stretching modes of the metal carbonyl complexes, $ML(CO)_5$, as a function of ligand oxidation state. Since metal carbonyl stretching frequencies are sensitive to changes in ligand electronic properties, it is possible that the carbonyl stretching frequencies in $LM(CO)_5$ will be influenced by ligand oxidation state. However, in the compounds examined in the present study, only very small changes in the intense E/A_1[1] band of the $LM(CO)_5$ complexes were observed; a shift of about 5 cm^{-1} to higher frequency occurred for each ferrocenyl group oxidized. This suggests that the coordinating ability of the ferrocenylphosphines is little changed upon oxidation of the ferrocenyl group or groups. This now raises the possibility of building molecules which contain charged, paramagnetic ligands and which, because of the charge, are soluble in more polar solvents and yet which retain properties much like normal phosphinemetal complexes.

Acknowledgements

We wish to express our appreciation for research grants and fellowships from the Research Corporation, the Joint Awards Council/University Awards Committee of the Research Foundation of the State University of New York, and to the Faculty Research Committee of SUNY-Oneonta. We are also indebted to Dr. Roberta G. Reed for her advice and assistance and to Professor M.D. Hawley of Kansas State University for assistance in the early stages of this project.

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