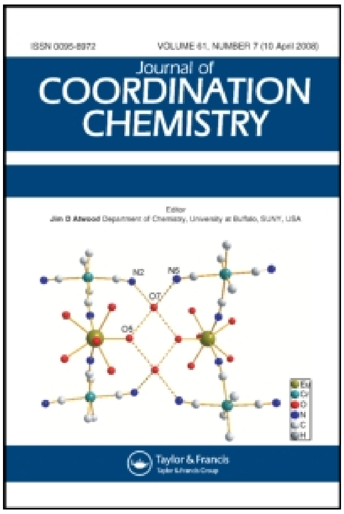

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Holy, Norman L. , Nalesnik, Theodore , Warfield, Larry and Mojesky, Mark(1983) 'METALLOCENE COMPLEXES OF CYCLOPENTADIENYL YLIDES', Journal of Coordination Chemistry, 12: 3, 157 — 162

To link to this Article: DOI: 10.1080/00958978308073844

URL: http://dx.doi.org/10.1080/00958978308073844

J. Coord. Chem., 1983, Vol. 12, pp. 157–162
0095–8972/83/1203–0157 $18.50/0

METALLOCENE COMPLEXES OF CYCLOPENTADIENYL YLIDES

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(Received April 30, 1982; in final form 23 May, 1982)

Several new transition metal complexes of the cyclopentadienyl ylides ($CpPPh_3$, $CpSMe_2$, and CpPy are reported. Reactions of $CpSMe_2$ with $MnCl_2$, $FeCl_2$, $CoCl_2$ and NiX_2 (where X = Cl or Br) leads to complexes in which the ylide:metal halide stoichiometry is 1:1. These complexes are assigned sandwich structures. Reaction of $Pd(NO_3)_2$ with $CpSme_2$ yields a very air-sensitive compound having a unique $(CpSMe_2)_3Pd(NO_3)_2$ stoichiometry. With HgX_2 the $CpSMe_2HgX_2$ (where X = Cl, Br, I) derivatives are formed; bonding of the mercury is shown for the iodide derivative to be at *C*-3 of the cyclopentadienyl ring. Reaction of $CpPPh_3$ with $FeCl_2$ produces two derivatives which appear to have stoichiometries unique in iron metallocene chemistry: $(CpPPh_3)Fe_2Cl_4$ and $(CpPPh_3)Fe_3Cl_4$.

INTRODUCTION

Wilkinson and coworkers[1] were the first to synthesize metal complexes of the cyclopentadienyl ylide $CpPPh_3$ when they reported the synthesis of $CpPPh_3M(CO)_3$ (M = Cr, Mo, W). Since that initial report several groups have investigated the preparation and reactions of several metal carbonyl derivatives.[2] Our own work has been principally with metal halides and our initial paper established that the Cp-Hg bonding in $(CpPPh_3HgI_2)_2$ was sigma in nature.[3] We have subsequently reported the preparation of other complexes of metal halides.[4] It is clear from published reports that cyclopentadienyl ylides have an unusually large range of bonding possibilities. Indeed, the Cp ring of $CpPPh_3$ may formally serve as a 2-electron,[3] 3-electron,[5] or 5-electron[2] donor. Not only are these complexes of synthetic and structural interest, but they also may have interesting catalytic[6] and toxicological[7] properties.

One of the features of $CpPPh_3$ is that the onium function is sterically large. It was considered that some interesting comparisons might be possible if complexes of an analogous ylide bearing a smaller onium function were prepared. Thus, our attention in this work has been directed mainly to the preparation of complexes of dimethylsulfoniumcyclopentadienylide, $CpSMe_2$.

RESULTS AND DISCUSSION

$CpSMe_2$ has an electronic structure similar to that of $CpPPh_3$, but differs substantially in steric requirements.[8] Only metal carbonyl complexes of $CpSMe_2$ have been reported previously.[9] We wish to report that reactions of anhydrous salts of first-row Group VIII divalent metal halides and $CpSMe_2$ in THF are almost instantaneous and lead to products with ylide: metal halide stoichiometries of 1:1. Most complexes listed in Table 1 are given dimeric formulae for structural reasons. Each synthesis was, of course, repeated several times to be certain of its reproducibility. The complexes are soluble only in coordinating solvents such as DMF or DMSO, and it has not been possible to recrystallize these complexes. Therefore, the elemental analyses listed in Table 1 are of unrecrystallized products. The most stable complex, that of $FeCl_2$, was examined in some detail, so

TABLE 1
Elemental analyses of new cyclopentadienyl metal complexes

Complex	Analysis Calcd. (Found) (%)						Colour
	C	*H*	*M*	*X*	*S/P*	*N*	
$(CpSMe_2)_2Mn_2Cl_4$	33, 36 (31, 66)	4, 00 (3, 71)	21, 80 (21, 71)				Grey
$(CpSMe_2)_2Fe_2Cl_4$	33, 24 (33, 14)	3, 98 (4, 28)	22, 08 (22, 04)	28, 03 (27, 98)	12, 68 (12, 64)		Tan
$(CpSMe_2)_2Co_2Cl_4$	32, 84 (31, 84)	3, 94 (3, 98)	23, 01 (23, 45)				Green
$(CpSMe_2)_2Co_2Br_4$	24, 37 (23, 84)	2, 92 (2, 94)	17, 08 (19, 42)				Lime
$CpSMe_2NiBr_2$	24, 39 (24, 50)	2, 92 (3, 76)	17, 03 (16, 53)				Green
$CpSMe_2HgCl_2$	21, 14 (21, 04)	2, 53 (2, 60)	50, 43 (50, 28)	17, 83 (17, 67)	8, 06 (7, 96)		Tan
$CpSMe_2HgBr_2$	17, 28 (17, 58)	2, 07 (2, 15)	41, 22 (41, 05)	32, 84 (32, 64)	6, 59 (6, 54)		Tan
$CpSMe_2HgI_2$	14, 48 (14, 68)	1, 74 (1, 72)	34, 55 (34, 45)	43, 71 (43, 79)	5, 52 (5, 29)		Yellow
$(CpSMe_2)_2Pd(NO_3)_2$	37, 57 (38, 64)	4, 50 (4, 73)	15, 85 (16, 02)				Red-Brown
$(CpSMe_2)_2RuCl_3$	36, 57 (34, 59)	4, 38 (4, 04)	21, 98 (22, 95)				Black
$(CpSMe_2)_2HfCl_4$	29, 36 (29, 22)	3, 52 (4, 02)	31, 16	24, 76 (23, 40)			White
$(CpPPh_3)Rh(NO_3)$	44, 90 (44, 04)	3, 11 (3, 30)	16, 72 (16, 43)		5, 74 (4, 94)	6, 83 (6, 70)	Tan
$(CpPPh_3)RuCl_3$	51, 18 (50, 08)	3, 55 (3, 44)	18, 72 (15, 88)				Brown
$(CpPPh_3)Fe_2Cl_4$	47, 64 (46, 73)	3, 30 (3, 82)	19, 26 (20, 72)				Brown
$(CpPPh_3)_3Fe_2Cl_4 \cdot 2THF$	67, 17 (67, 73)	5, 34 (5, 62)	8, 12 (8, 11)				Dark Red
$CpPyFeCl_3$	44, 48 (44, 33)	3, 36 (3, 79)	26, 68 (20, 70)	26, 26 (26, 19)		5, 18 (5, 18)	Brown
$CpPyHgCl_3$	28, 96 (29, 73)	2, 19 (2, 33)	48, 23 (48, 83)				Tan

discussion will be focused there. For the iron complex two structural possibilities have been considered most likely.

$$MX_2 + CpSMe_2 \longrightarrow (CpSMe_2)MX_2 \quad (MX_2 = MnCl_2, CoCl_2, FeCl_2, NiCl_2, NiBr_2)$$

In (1) the octahedral iron would most likely be high spin. Considering "spin only" contributions, the structure would be predicted to have a magnetic moment of about 5.1 BM per iron. For (II), while the cation would be diamagnetic, the anion would be tetrahedral and have a spin of ca 5.1 BM. The experimental value, determined at room temperature, is 2.5 BM per iron atom, or 5.0 BM if only one iron has a magnetic moment. This value clearly supports (II). Additional evidence for (II) is provided by cyclic volta-

TABLE 2
Cyclic voltametry of iron metallocenes

Complex	E_{pc}	E_{pa}
Cp_2Fe	0.23	0.35
$(CpSMe_2)_2Fe\ FeCl_4$	0.22	0.31

metry. In aqueous acetonitrile the curve for the ylide complex (Table 2) was almost identical in shape and potentials with that for Cp_2Fe. The constant peak current ratio, ip, c/ip, a = 1.0 ± 5%, at scan rates from 25 to 250 mVs^{-1} indicate stability for the oxidized $[(CpSMe_2)_2Fe]^{3+}$ form. The UV spectroscopy is also in agreement with (II).[8] The electronic structure of the ylide $CpSMe_2$ may be considered to consist of two mesomers, the "ylide" and the "ylene", with the former predominating.

In the UV spectrum of the ylide it is possible to assign transitions attributable to each mesomer.[8b] The "*ylide*" mesomer is assigned to a transition at 195 nm (MeOH) and the "*ylene*" mesomer a $\pi \rightarrow$ CT absorption at 273 nm. For a pentahapto complex it would be anticipated that the metal would alter the electronic nature of the ylide. In the ylide ferrocene complex, with η^5-bonding, it would be anticipated that the "ylide" mesomer would be enhanced at the expense of the ylene mesomer.[10] The UV spectrum of the complex (MeOH) revealed the π-CT band to be considerably diminished in comparison with the π-π^* band, in agreement with η^5 coordination. Absorption values are not given because the solutions were not completely stable.

A further argument for a classical ferrocene structure is that of analogy. The ligand $CpCN^-$, a cyclopentadienyl ligand also bearing an electron-withdrawing group is considered to have a ferrocene structure.[11] All efforts to grow crystals have failed. Solutions of the complex darken considerably after a few hours.

The Ni(II) halide derivatives of $CpSMe_2$ were prepared by dropping a 1,2-dimethoxyethane (DME) solution of the nickel salts into a DME solution of the ylide. DME was employed because of the greater solubility of the $NiCl_2$ and $NiBr_2$ salts. A light green precipitate formed immediately; the melting points for both derivatives were over 300 C. The solid was only slightly air-sensitive, but solutions (DMF) decomposed rapidly.

$$2\,NiX_2 + 2\,CpSMe_2 \longrightarrow [(CpSMe_2)_2Ni]^{2+}\,[NiX_4]^{2-} \quad X = Cl, Br$$

A sandwich structure is favoured, but the detailed bonding is not clear. The $[NiCl_4]^{2-}$ ion has a magnetic value of 3.7-4.0 BM, depending on its nearness to perfect T_d symmetry. Cp_2Ni has a value of 2.86 BM. Measurement of the value for the ylide complex revealed a value of 2.1 BM/Ni^{2+}. Assigning a normal value for $[NiCl_4]^{2-}$ requires that the cation be nearly diamagnetic. Efforts to replace the anion have been unsuccessful. Thus, there is uncertainty in the magnetic value for the cation. Certainly the value is less than that expected for a strict analog of Cp_2Ni. There are two obvious possibilities for the low magnetic value. Cp_2Ni is described as a 20-electron complex with single electrons occupying degenerate e_{1g}^{*} orbitals. The e_{1g}^{*} orbitals stem partially from ligand wave functions which are degenerate in the case of cyclopentadienyl,[12] but not degenerate for the ylide.[8b] Thus, in the ylide complex the e_{1g}^{*} orbitals could be split. There is an alternate interpretation. Perhaps one ring is pentahapto to the metal and the other is trihapto; such a bonding pattern would produce a complex having a formal 18-electron configuration. Conclusive evidence concerning the ordering of molecular orbitals would most dependably be obtained from temperature-dependent magnetic studies, but appropriate equipment was not available.

The generality of the reaction of $CpSMe_2$ with second or third-row metal halides has been but briefly explored. Only one second-row Group VIII complex, that of $RuCl_3$, and one of Group VI were investigated. The stoichiometries of these complexes are analogous to those of Cp_2RuCl and Cp_2HfCl_2. It will be noted that the $CpPPh_3$ complex of $HfCl_4$ has a $(CpPPh_3)HfCl_4$ stoichiometry;[4a] this stoichiometry difference is likely to be related to the insolubility of the $(CpPPh_3)HfCl_4$ complex.

$$2\ CpSMe_2 + MCl_x \longrightarrow (CpSMe_2)_2MCl_x \quad MCl_x = RuCl_3,\ HfCl_4$$

The mercuric halide derivatives of $CpSMe_2$ are readily formed by adding dropwise a THF solution of the appropriate mercury halide salt into a THF solution of the ylide. After a few minutes pentane was added and the precipitate collected. The derivatives are relatively air-stable. Crystals of the iodide suitable for a structural determination were grown in THF. We were particularly interested in the location of the mercury, whether it was at *C*-3 of the Cp ring, the same position as in the $CpPPh_3HgI_2$ derivative, the *C*-1 position, which, if analogous to $CpPPh_3$, would have the highest electron density,[12] or at *C*-2, the position where substitution occurs exclusively.[13] The mercury atom was found to be bonded at the *C*-3 position.[14] Thus the bonding of mercury at *C*-3 is favoured even when the onium function is relatively small sterically.

We considered that the ylide $CpSMe_2$ might provide access to an analog of the elusive "palladocene". Wilkinson first described the reaction of Cp^- with Pd^{2+}, but the product could not be characterized as Cp_2Pd; rather it appeared more likely to be polymeric.[15] This was not surprising since palladium does not readily form octahedral or pseudo-octahedral complexes. A $CpPPh_3PdL$ ($L = C_4(CO_2Me)_4$) complex was found by Pierpont to have a π-allyl bond between the metal and the ylide,[4] and it was considered that $CpSMe_2$ might be particularly favourable for forming $(CpSMe_2)_2Pd^{2+}$ salts in which one or both ylides were bonded in a π-allyl manner. Adding a THF solution of $Pd(NO_3)_2$ to a THF solution of $CpSMe_2$ results in the immediate precipitation of a brown-red product. This complex is highly air-sensitive. Elemental analysis revealed not a $(CpSMe_2)_2Pd(NO_3)_2$ stoichiometry but rather one of $(CpSMe_2)_3Pd(NO_3)_2$. Again spectral data have been difficult to obtain. A UV spectrum does show a broad absorption between 200 nm and 290 nm and suggests a variety of bonding modes. We suggest structure (III) based on known $CpPdL_2$[16] and Cp_3Ti[17] models.

CpPy is an ylide similar to $CpSMe_2$ in the sense that it has minimal steric requirements, but it has a very different electronic structure in that the "ylene" mesomer is significantly more important than it is in $CpSMe_2$.[18]

$$2\ Cp\text{-}Py + 2\ FeCl_2 \longrightarrow (Cp\text{-}Py)_2Fe_2Cl_4$$

Complexes with $FeCl_2$ and $HgCl_2$ have the same stoichiometries as those derived from $CpSMe_2$.

In our previous papers on complexes of $CpPPh_3$ the metal halides were selected from Groups IIB, IVB, and VIB. We sought to expand these investigations, especially to prepare complexes of metals further to the right in the periodic table. The initial result with a first-row, Group VIII metal was not encouraging. When a THF solution of $CoCl_2$ was added to a THF solution of $CpPPh_3$ at −78°, a green precipitate was formed. This precipitate was very thermolabile and decomposed above −40°. Because of this thermal instability attention was directed to possible complexes of $FeCl_2$. Since anhydrous $FeCl_2$ (as the $FeCl_2 \cdot 1.45$ THF complex) has limited solubility in THF, the salt and the ylide were stirred in THF for several days. After one day the colorless $FeCl_2$ was partially consumed and a brown precipitate began to appear. After three days the mixture was filtered in a Schlenk tube and the brown product collected. Elemental analysis established the stoichiometry as $(CpPPh_3)Fe_2Cl_4$. This stoiciometry appears to be unique in metallocene chemistry. The compound is indefinitely stable at room temperature and but mildly air-sensitive. It is soluble only in good coordinating solvents like DMF or DMSO. A ^{31}PNMR spectrum of this compound in DMF displays a single narrow absorption at 25.9 ppm; the uncoordinated ylide absorbs at 13.1 ppm ($CDCl_3$). On the basis of the ^{31}PNMR spectrum the complex appears to be diamagnetic.

A second product was isolated from this reaction by adding pentane to the filtrate. This complex is dark-red and highly air-sensitive. It is insoluble in nonpolar solvents but soluble in THF and DMF. A ^{31}PNMR spectrum also displays a single narrow phosphorus peak at 13.2 ppm (THF), virtually unshifted from the absorption of the starting ylide. Elemental analysis reveals a $(CpPPh_3)_3Fe_2Cl_4$ stoichiometry.

Reactions of metal halides with cyclopentadienyl ylides are very general. Based upon known reactions, it would appear that many additional complexes could be prepared. Typically structures of these complexes parallel those of cyclopentadienyl. Differences in the detailed bonding descriptions between classic Cp_2M and ylide metallocenes are evident; this is clear from our Ni^{2+}-$CpSMe_2$ complex. With the bulky -PPh_3 onium group the iron(II) derivatives do not form complexes having structures analogous to Cp_2Fe, and it would appear that other 1st row transition metals also form complexes of novel stoichiometry. Reactions of lanthanides or actinides with these ylides are untested.

Acknowledgements. The partial support of the Petroleum Research Fund, administered by the American Chemical Society, the Alexander von Humboldt-Stiftung, and of the Faculty Research Committee, Western Kentucky University are acknowledged. The efforts of Lisa Del Buono, Terry Goolsby, Rick Fowler, and Dr. John Riley are appreciated. Dr. Melvin Joesten, Department of Chemistry, Vanderbilt University, kindly measured the magnetic moments.

EXPERIMENTAL

General Data. Ultraviolet spectra were of methanol solutions and were recorded on a Cary 14 spectrophotometer. Cyclic voltammetry was of a 10^{-3} M $(CpSMe_2)_2Fe_2Cl_4$ solution in 67% aqueous acetonitrile (containing 0.33 M KNO_3 as electrolyte), carbon paste vs SCE. Elemental analyses were performed by Galbraith Laboratories or by the Technische Universität, München. $CpPPh_3$, $CpSMe_2$ and CpPy were prepared according to literature methods.[19] Melting points were above 300° and thus are not recorded. All solvents were dried and distilled.

General Procedure for $CpSMe_2$ and CpPy Derivatives. A standard procedure was employed for the preparation of derivatives. A THF solution of the metal halide (in 10% molar excess) was added to a THF solution of the ylide. Precipitation was instantaneous. The precipitate was collected by filtration and washed with a small amount of THF. All operations were carried out under nitrogen. Yields were 70-100%. This procedure is illustrated by that used to synthesis the $FeCl_2$ derivative.

Bis-(η^5-dimethylsulfoniumcyclopentadienylide)iron(II) tetrachloroferrate(II). To a solution of 0.76 g (6.00 mmol) of dimethylsulfoniumcyclopentadienylide in 50 cm^3 of dry THF was added a 400 cm^3 THF solution containing 0.87 g (6.60 mmol) of $FeCl_2 \cdot 1.45$ THF. The reaction was performed at room temperature. A light brown precipitate formed immediately; this was collected by filtration and washed with 20 cm^3 THF. The precipitate was dried *in vacuo* for 3 hr. Yield, 1.50 g (97%). Melting point, slow decomposition between 300 and 500° (under N_2).

Reaction of Triphenylphosphoniumcyclopentadienylide with $FeCl_2$. Triphenylphosphoniumcyclopentadienylide (0.70 g, 2.2 mmol) and 0.66 g (5.0 mmol) of $FeCl_2\cdot1.45$ THF were combined in 25 cm^3 of dry THF. After stirring for three days a brown precipitate had formed; this was filtered and washed three times with 20 cm^3 portions of THF. The precipitate was dried for 3 hr *in vacuo* at 140°. Yield 0.35 g (27%) of $(CpPPh_3)Fe_2Cl_4$, melting point 160-170° (dec). ^{31}PNMR (DMF); 25.9 ppm, s. To the combined filtrate and washings was added pentane. A red precipitate formed immeidately; this was collected by filtration, washed with 10 cm^3 of THF and dried *in vacuo.* Yield 0.70 g (69%) of $(CpPPh_3)_3Fe_2Cl_4\cdot2THF$, melting point 220-235° (dec). ^{31}PNMR (THF); 13.2 ppm, s.

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