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Synthesis and electrochemical aspects of group 14 iron complexes of the type $(\eta^5-C_5H_5)Fe(L)_2ER_3$, $L_2 = (CO)_2$, $(Ph_2P)_2CH_2$; E = C, Si, Ge, Sn

Note

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Dedicated to Prof. Piero Zanello.1

Abstract

The dicarbonyl and diphosphine complexes of the type $(\eta^5-C_5H_5)Fe(L)_2ER_3$ ($L_2 = (CO)_2$ (**a**), $(Ph_2P)_2CH_2$ (**b**); $ER_3 = CH_3$ (1a/b); SiMe₃ (2a/b), GeMe₃ (3a/b), SnMe₃ (4a/b)) were synthesized and studied electrochemically. Cyclic voltammetric studies on the dicarbonyl complexes 1a-4a revealed one electron irreversible oxidation processes whereas the same processes for the chelating phosphine series 1b-4b were reversible. The E_{ox} values found for the series 1a-4a were in the narrow range 1.3-1.5 V and in the order Si > Sn \approx Ge > C; those for 1b-4b (involving replacement of the excellent retrodative π -accepting CO ligands by the superior σ -donor and poorer π -accepting phosphines) have much lower oxidation potentials in the sequence Sn > Si \approx Ge > C. This latter oxidation potential pattern relates directly to the solution ³¹P NMR chemical shift data illustrating that stronger donation lowers the E_{ox} for the complexes; however, simple understanding of the trend must await the results of a current DFT analysis of the systems. © 2007 Elsevier B.V. All rights reserved.

Keywords: Cyclic voltammetry; Diphosphine; Group 14 elements; Retrodative bonding

1. Introduction

The varying elements of group 14, C, Si, Ge, Sn and Pb, ranging from non-metal via metalloid to metal, represent an entertaining area of the Periodic Table. We are interested in their properties when directly bonded to transition metals and have found the metal substituent $(\eta^5-C_5H_5)Fe(CO)_2$ (Fp) a rewarding source of new chemistry [1]. The electrochemistry of some complexes of this type, FpER₃, R = group 14 element are scattered in the literature and in general Fp derivatives exhibit irreversible oxidations [2,3]. However, substitution of the carbonyl groups by phosphine ligands, especially those

with chelating diphosphino substituents has been reported to exhibit a greater degree of reversibility [3]. Recently, $(\eta^5-C_5Me_5)Fe(dppe)X$ complexes (dppe = bis-(diphenylphosphino)ethane, X = F, Cl, Br, I, H, CH₃) have been studied theoretically as well as experimentally in terms of the Fe–X bond energy and the electrochemical oxidation [4]. Cyclic voltammetry of these complexes revealed a reversible redox process and the electrode potential for the [Fe–X]^{II/III} couple decreased in the order $I > Br > Cl > H > F > CH_3$. This trend is the opposite of that predicted on the basis of halide electronegativity alone, and suggested the importance of π -donation from halide to metal, a suggestion corroborated by DFT calculations.

In the present article, we report an electrochemical study of the complexes $(\eta^5-C_5H_5)Fe(CO)_2ER_3$ and $(\eta^5-C_5H_5)-Fe(dppm)ER_3$, $ER_3 = CH_3$, $SiMe_3$, $GeMe_3$, $SnMe_3$; dppm = bis(diphenylphosphino)methane.

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¹ Piero: Congratulations on your fine contributions. Cheers, Keith.

2. Results and discussion

Synthesis: The known compounds **1a–4a** were prepared from the direct reaction of Fp–Na and iodomethane (for **1a**) and corresponding trimethylchlorosilane/germane/ stannane (for **2a–4a**). In turn, as shown in Scheme 1, compounds **1b–4b** were synthesized in 70–80% yield by photochemical treatment of **1a–4a** with an equimolar amount of dppm. The substitution of the carbonyl groups was monitored by infrared and ³¹P NMR spectroscopy. We observed that the first carbonyl group replacement takes 10–15 h, while 40–50 h were taken to replace both the carbonyl groups. Each of **1b–4b** were isolated as crystalline solid materials and characterized by ¹H, ¹³C, ³¹P, ²⁹Si, ¹¹⁹Sn NMR and elemental analysis.

2.1. Spectroscopic characterization

NMR spectroscopic data authenticated the molecular formulation of 1b-4b, and in the case of 1b being in agreement with the literature values [5]. For example, ¹³C NMR spectroscopic analysis revealed a significant upfield shift of the η^5 -C₅H₅ carbons of all Nb complexes ($\Delta \delta \sim 8 \text{ ppm}$ when compared to the corresponding dicarbonyl precursors, Na). The ²⁹Si NMR spectroscopic data for 2b exhibited a triplet at 27.6 ppm $({}^{2}J_{Si-P} = 43.3 \text{ Hz}) \sim 14 \text{ ppm}$ upfield relative to 2a (²⁹Si $\delta = 41.8$ ppm) which is similar to the published value $\delta = 25.1$ ppm, ${}^{2}J_{Si-P} = 46$ Hz] for $(\eta^5-C_5H_5)Fe(dppe)SiMe_3$ [6]. Similarly an upfield triplet at 69.0 ppm $[^2J_{\text{Sn-P}} = 447 \text{ Hz}]$ was observed in ¹¹⁹Sn NMR of 4b, representing a $\Delta\delta$ value of 73 ppm. The uncoupled ³¹P NMR spectrum of each compound revealed a singlet in the range of 37–50 ppm, downfield (48–70 ppm) compared to the free ligand $[\delta^{31}P (dppm) = -21 ppm]$.

2.2. Cyclic voltammetric studies

Electrochemical study of **1a–4a** and **1b–4b** was conducted in order to establish a correlation among the group 14 elements in the present class of compounds. At the scan rate of 50 mV s⁻¹ **1a–4a** exhibited an irreversible oxidation and E_{ox} (V) was found as follows: 1.335 (**1a**), 1.421 (**2a**), 1.401 (**3a**) and 1.403 (**4a**). This is a narrow range in the order of Si > Sn \approx Ge > C. Fig. 1 shows a plot between electronegativity and E_{ox} for **1a–4a** which reveals that by





Fig. 1. A plot between E_{ox} vs. EN (Pauling) for CpFe(CO)₂ER₃ (E = C, R = H; E = Si, Ge, Sn, R = Me) [1a-4a].

decreasing the electronegativity of E in ER₃, the oxidation potential increases [EN (Pauling) = 2.55 (C), 1.90 (Si), 2.01 (Ge) and 1.96 (Sn)] [7], a counterintuitive result.

Many $(\eta^5-C_5H_5)Fe(CO)_2$ -X complexes have been studied by Mossbauer, IR, and multinuclear NMR spectroscopy [8]. From these studies it has been suggested a small component of retrodative π -bonding between the metal atom and the silicon/tin exists in complexes of type $(\eta^5-C_5H_5)Fe(CO)_2SiR_3$ [8b] as well as in $(\eta^5-C_5H_5)Fe(LL')_2SnR_3$ [LL' = CO, L = CO; L' = PPh₃] [8a,8c]. The pattern in **1a**-**4a** for oxidation potential data may be analyzed in terms of the variable presence of such retrodative bonding. In the case of $(\eta^5-C_5H_5)Fe(CO)_2CH_3$ retrodative bonding by the alkyl group is non-existent and its strong σ -donor character, observed on the basis of Mossbauer studies result in a lower E_{ox} .

At a similar scan rate the chelating phosphine complexes, **1b**–**4b** exhibited a single one electron reversible oxidation at much lower oxidation potentials in the greater range -0.1–0.32 V, Table 1, Fig. 2. This change is anticipated for the replacement of the strongly retrodative π -bonding carbonyl ligands by the less effective π -bonding, and superior σ -donating, diphosphine. Such a replacement results in a build-up of electron-density at iron, facilitating the oxidation process [2]. The oxidation potential sequence of **1b**–**4b** exhibits an order of Sn > Si > Ge > C.

Table									
Cyclic	voltammetric	data	of	1a–4a	and	1b-4b	in	CH_2Cl_2	(0.1 M
[BILN]	BE ₄) ^a								

Compound	$E_{\rm ox}$ (V)	$E_{\rm red}$ (V)	$E_{1/2}$ (V)	$\Delta E_{\rm p} \left({\rm V} \right)$					
1a 1b	1.335 -0.110	-0.236	-0.173	0.126					
2a 2b	1.421 0.174	-0.007	0.083	0.181					
3a 3b	1.401 0.163	-0.016	0.073	0.179					
4a 4b	1.403 0.319	-0.011	0.154	0.330					

Sweep rate 50 mV s^{-1} .

^a References with AgCl/Ag.

Scheme 1.



Fig. 2. A representative cyclic voltammogram of 1b.

A useful tool for evaluating electronic effects of substituents is the Taft (σ^*) coefficient [9]. As may be seen from Fig. 3, a plot of the various E_{ox} values against the Taft (σ^*) values results in another inverse linear relationship but as with the electronegativity relationship noted above, this relationship is opposite to that predicted, i.e. more electron-donating substituents result in higher E_{ox} values. An interesting correlation between ³¹P NMR and E_{ox} values in 1b-4b revealed that they are also linearly related. Complex 1b exhibited the strongest coordination between P and Fe (³¹P NMR $\Delta \delta \sim 70$ ppm) which directly relates to the increased electron-density at the iron center, resulting in easier oxidation. For complexes 2b-4b there is apparently weaker P coordination to the iron atom as noted by the shifting ³¹P resonances (³¹P NMR $\Delta \delta \sim 55-60$ ppm) and elevated E_{ox} values. These data strongly suggest that for the complexes 1b-4b the donor function of the diphosphine controls the E_{ox} values.

From both the series **1a**–**4a** and **1b**–**4b** a general pattern of carbon giving the lowest oxidation potential an argument could be put forward that retrodative π -bonding is important to differing extents for the Si, Ge and Sn substituents and explains the inability of both simple electronegativity and Taft coefficients relationships to hold. Such an explanation is analogous to that proposed for the related diphosphine derivatives of $(\eta^5-C_5Me_5)Fe(dppe)X$, (X =



Fig. 3. A plot between E_{ox} vs Taft constant (σ^*) for CpFe(PP)ER₃ (E = C, R = H; E = Si, Ge, Sn, R = Me) [1b–4b].

F, Cl, Br, I, H, CH₃) on the basis of theoretical calculations and the involvement of π -donation (π -dative bonding) in the order F > Cl > Br > I [4].

We are engaged in DFT calculations on the complexes 1–4, and cyclic voltammetric analysis of other transition metal systems containing direct bonds to C, Si, Ge and Sn to provide a more concise set of arguments for our observed experimental data. Whereas oxidation of the dicarbonyl complexes 1a–4a can involve loss of an electron from a Fe–E bonding HOMO [10], that from the complexes 1b–4b can be from a corresponding σ^* orbital with more metal *d* content.

2.3. Experimental procedure

All experiments were performed under an atmosphere of dry N₂ using Schlenk techniques. THF and hexanes were freshly distilled from sodium benzophenone ketyl immediately prior to use. 1a-4a were synthesized according to the literature method [11]. Other chemicals were purchased from Aldrich and used as received. Cyclic voltammetric measurements were performed using a Perkin-Elmer potentiostat/galvanostat CV (model # 263A) analyzer. The electrochemical cell comprised a platinum wire working electrode, a silver wire reference electrode, and platinum wire counter electrode. All measurements were made in dry N₂ atmosphere. E_{ox}/E_{red} was referenced to Ag/AgCl couple. Infrared spectra were obtained in THF solution on an ATI Mattson infinity series FTIR; ¹H, ¹³C, ²⁹Si, ¹¹⁹Sn and ³¹P NMR was recorded on a Bruker DPX-300 at 300, 75.4, 59.6, 111.8 and 121.5 MHz respectively. Elemental analysis was performed at Galbraith Laboratories.

2.3.1. Synthesis of $(\eta^5 - C_5 H_5) Fe(dppm) Me$ (1b)

To a 25 mL THF solution of **1a** (0.5 g, 1.17 mmol) in a quartz tube was added (0.45 g, 1.18 mmol) of dppm and the tube was degassed twice. The solution was then irradiated by a Hanovia 450 W medium pressure lamp at a distance of 4 cm for two days. The progress of the photochemical reaction was monitored by infrared and ³¹P NMR spectroscopy. After completion of the reaction THF was evaporated under vacuum. The solid material obtained was washed with hexanes and filtered. The hexane insoluble material was collected, dried and characterized as **1b.** Recrystallization from benzene and hexanes (1:2) afforded an analytically pure compound in 64% yield. Complexes 2b-4b were prepared following the identical procedure as described above for 1b in 60% (2b), 67% (3b) and 75% (4b) yields, respectively. Spectroscopic data for 1b was reported elsewhere [5] and compared well with the present data.

2.3.2. $(\eta^5 - C_5 H_5) Fe(dppm) SiMe_3$ (2b)

Anal. Calc. for $C_{33}H_{36}P_2SiFe: C, 68.51; H, 6.22.$ Found: C, 68.22; H, 6.03%. ¹H NMR: δ 0.36 (s, 9H, SiMe₃), 4.41 (s, 5H, Cp), 3.90 (2H, CH₂), 7.00–7.51 (20H, Ph). ¹³C NMR: δ 8.89 (SiMe₃), 76.0 (Cp), 43.8 (CH₂, $J_{P-C} = 18$ Hz) 128.9, 130.8, 130.9, 139.3 (Ph). ³¹P NMR: δ 40.5. ²⁹SiNMR: δ 27.6 (t, ² $J_{Si-P} = 43.3$ Hz).

2.3.3. $(\eta^{5}-C_{5}H_{5})Fe(dppm)GeMe_{3}$ (**3b**)

Anal. Calc. for $C_{33}H_{36}P_2GeFe$: C, 63.56; H, 5.77. Found: C, 63.57; H, 5.77%. ¹H NMR: δ 0.32 (s, 9H, GeMe₃), 3.90 (q, 2H, CH₂), 4.35 (s, 5H, Cp), 7.00–7.46 (20H, Ph). ¹³C NMR: δ 7.28 (GeMe₃), 44.0 (t, CH₂, $J_{P-C} = 18$ Hz), 75.2 (Cp), 129.1, 131.0, 139.5, 142.0 (Ph). ³¹P NMR: δ 40.3.

2.3.4. $(\eta^5 - C_5 H_5) Fe(dppm) SnMe_3$ (4b)

Anal. Calc. for $C_{33}H_{36}P_2SnFe: C, 59.10; H, 5.37.$ Found: C, 58.63; H, 5.36%. ¹H NMR: δ 0.13 (s, 9H, SnMe₃), 3.90 (q, 2H, CH₂), 4.33 (s, 5H, Cp), 7.03–7.43 (20H, Ph). ¹³C NMR: δ –4.2 (SnMe₃), 45.2 (CH₂, $J_{P-C} = 18$ Hz), 73.3 (Cp), 128.2, 131.3, 140.1, 142.3 (Ph). ³¹P NMR: δ 37.8. ¹¹⁹SnNMR: δ 69.0 (t, ² $J_{Sn-P} = 447$ Hz).

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