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Electron Spin Resonance Spectra of Copolymer-Attached Trichloro(η^5-cyclopentadienyl)niobium and Copolymer-Attached Dichlorobis(η^5-cyclopentadienyl)niobium

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Stewart and Porte[1] have reported ESR spectra of some bis(π-cyclopentadienyl) compounds, including dichlorobis(η-cyclopentadienyl)niobium in chloroform–ethanol (9:1) glass at −196 °C. The spin Hamiltonian

$$\hat{\mathcal{H}} = \beta_e[g_{xx}H_x\hat{S}_x + g_{yy}H_y\hat{S}_y + g_{zz}H_z\hat{S}_z] + T_{xx}\hat{I}_x\hat{S}_x + T_{yy}\hat{I}_y\hat{S}_y + T_{zz}\hat{I}_z\hat{S}_z \quad (1)$$

was used[3] in interpreting these spectra.

In this work, ESR spectra of trichloro(η^5-cyclopentadienyl)niobium attached to 20% cross-linked styrene–divinylbenzene copolymer beads (hereafter referred to as copolymer-attached $CpNbCl_3$) and dichlorobis(η^5-cyclopentadienyl)niobium, also attached to 20% cross-linked styrene–divinylbenzene copolymer beads (hereafter referred to as copolymer-attached Cp_2NbCl_2), have been obtained. Spin-Hamiltonian parameters have been determined from these experimental spectra.

Experimental Section

Samples of copolymer-attached $CpNbCl_3$ and copolymer-attached Cp_2NbCl_2 were obtained from Chak-po Lau. Syntheses of these compounds have been described by Lau and by Lee and Brubaker.[2]

Portions of these compounds were transferred into Pyrex tubes in an argon-filled glovebox. After being sealed, these tubes were used as ESR sample tubes. (The ESR absorption due to Pyrex occurs at magnetic field strengths very different from those at which these samples absorb, as Pyrex glass exhibits apparent *g* values of 6.2 and 4.2.)[3]

ESR spectra to be used for quantitative interpretation were obtained by using a Varian V-4500-10A EPR spectrometer. A Hewlett-Packard frequency converter and electronic counter were used to determine microwave frequency accurately. A proton marker was used to determine magnetic field values accurately. ESR spectra were obtained in sections. A typical scan covered only 200–250 G—sometimes less—of the total magnetic field range. Neither of the spectra obtained for quantitative interpretation was obtained entirely in one session. The microwave frequency during a given session was often slightly different from microwave frequencies during other sessions.

For quantitatively interpreted spectral portions for copolymer-attached $CpNbCl_3$, the microwave frequency was between 9.098 and 9.111 GHz. The observed variations in microwave frequency could lead to errors of approximately 0.002 in **g** tensor values and approximately 0.000 04 cm^{-1} in hyperfine tensor values. Some calculated corrections were applied to compensate somewhat for these variations.

The sample temperature was maintained at −126 °C while spectra to be interpreted quantitatively were obtained. This temperature was used for both copolymer-attached $CpNbCl_3$ and copolymer-attached Cp_2NbCl_2. This temperature was determined by calibration with a thermocouple under conditions similar to those in effect when ESR spectra were being obtained for quantitative interpretation. When those quantitative ESR spectra were being obtained, no thermocouple was used; instead, a temperature dial setting and nitrogen gas flow rate corresponding to those used in calibration were employed consistently.

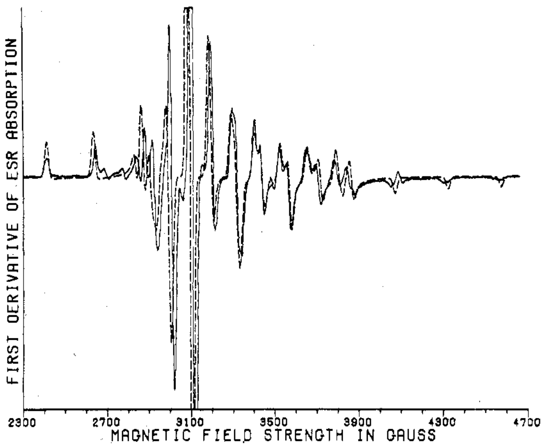

Figure 1. Experimental and simulated ESR spectra of copolymer-attached $CpNbCl_3$.

Data obtained when a standard sample of pitch in KCl was used indicated an error of 0.01% in microwave frequency to magnetic field strength ratio and/or in the procedure used to determine the magnetic field strength of the ESR absorption from a spectrum on chart paper.

Magnetic field strengths were determined at selected points on piecewise experimental spectra. These selected points included relative extrema and points whose vertical coordinates were halfway between those of consecutive relative extrema. Many of these magnetic field strengths were compared later with corresponding values from simulations.

The sections of spectra obtained for accurate interpretation do not provide as aesthetically excellent pictures as desired for illustrations. The illustrated experimental ESR spectra were obtained by use of a Varian E-4 EPR spectrometer, which is a different instrument from the one with which very accurate work was done.

For quantitative spectral portions for copolymer-attached Cp_2NbCl_2, the microwave frequency was between 9.1081 and 9.1092 GHz. This uncertainty of 0.0011 GHz could contribute uncertainties of about 0.0003 to the diagonal elements of the **g** tensor and uncertainties of about 0.000 005 cm^{-1} to the diagonal elements of the hyperfine tensor.

If the magnetic field strengths read from chart paper were perfectly accurate, then the microwave frequency was 9.197 ± 0.010 GHz for the experimental ESR spectrum of copolymer-attached Cp_2NbCl_2 at −126 ± 4 °C shown in Figure 2. For this scan, the magnetic field strengths read from chart paper do seem to be reliable to within 10 G and have been accepted for use in Figure 2.

Results and Discussion

The ESR spectra obtained for both copolymer-attached $CpNbCl_3$ and copolymer-attached Cp_2NbCl_2 are powder pattern spectra; that is, each of these experimental spectra could be considered a superposition of spectra for paramagnetic centers at many orientations relative to the magnetic field. Equations[4,5] appropriate for simulating powder pattern ESR spectra have been incorporated into computer programs that have been written to enable simulation of such spectra and generation of simulated data that can be compared readily with experimental data.

Solutions[4,5] appropriate for the spin Hamiltonian given by eq 1 were used in calculating spectra. The **g** tensor axes have been assumed identical with the corresponding hyperfine (**T**) tensor axes.

For each of these two compounds, the hyperfine parameters T_{xx}, T_{yy}, and T_{zz} all have the same sign. This sign was not determined but is assumed to be negative.

Experimental (solid line) and calculated (dashed line) ESR spectra are presented in Figures 1 and 2. For each compound, a systematic deviation seems to occur near the center of the spectrum. This deviation could be due to a quadupole inter-

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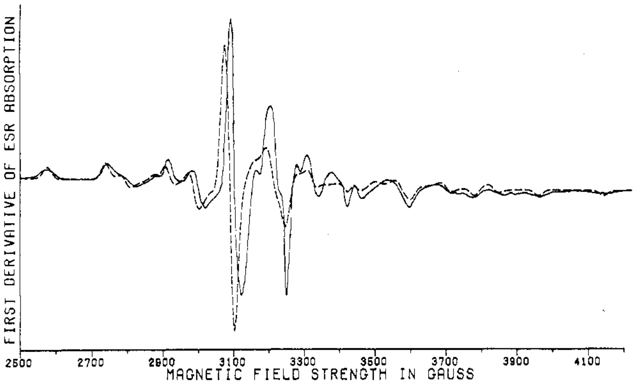

Figure 2. Experimental and simulated ESR spectra of copolymer-attached Cp_2NbCl_2.

Table I. Spin-Hamiltonian Parameters

	copolymer-attached		
	$CpNbCl_3$[a]	Cp_2NbCl_2[a]	Cp_2NbCl_2[b]
g_{xx}	1.981 ± 0.002	1.976 ± 0.002	1.980 ± 0.0005
g_{yy}	1.990 ± 0.002	1.952 ± 0.002	1.940 ± 0.0005
g_{zz}	1.908 ± 0.002	2.017	2.000 ± 0.001
T_{xx}[c]	−0.0105 ± 0.0001	−0.0106 ± 0.0001	−0.010 66 ± 0.000 02
T_{yy}[c]	−0.0093 ± 0.0001	−0.0159 ± 0.0001	−0.015 98 ± 0.000 02
T_{zz}[c]	−0.0214 ± 0.0001	(−0.005 28)	−0.005 28 ± 0.000 02
ref	this work	this work	3

[a] At −126 °C. [b] In chloroform–ethanol (9:1) glass at −196 °C. [c] In cm^{-1}.

action that is not included in eq 1. If an uncalculated quadrupole interaction is indeed present, then failure to include it in determining spin-Hamiltonian parameters could lead to errors of approximately 0.000 05 cm^{-1} in principal values of the hyperfine tensor but to no significant errors in the principal values of the **g** tensor.

Principal values of the **g** and hyperfine (T) tensors for copolymer-attached $CpNbCl_3$ and copolymer-attached Cp_2NbCl_2 are listed in Table I. Overall estimated uncertainties also are given. For copolymer-attached $CpNbCl_3$, the x and y patterns might be interchanged. There do not seem to be enough resolved features of the z pattern of copolymer-attached Cp_2NbCl_2 to permit a confident and precise determination of g_{zz} and T_{zz}. The values of g_{zz} and T_{zz} still are regarded as unknown; however, their input values used in obtaining the calculated copolymer-attached Cp_2NbCl_2 spectrum are given in parentheses. For comparison, spin-Hamiltonian parameters reported by Stewart and Porte[1] for dichlorobis(η^5-cyclopentadienyl)niobium (Cp_2NbCl_2, not attached to any polymer) in chloroform–ethanol (9:1) glass at −196 °C are also given in Table I.

The analyses of the spectra strongly support the identities and assumed structures of the two copolymer-supported Nb(IV) species. The supported Cp_2NbCl_2 must have the same structure as the unsupported compound and the $CpNbCl_3$ a "piano stool" structure with a "local" C_{3v} axis through the three chlorine atoms. The unsupported $CpNbCl_3$ is unknown.

Registry No. $CpNbCl_3$, 71463-31-5; Cp_2NbCl_2, 12793-14-5; styrene–divinylbenzene copolymer, 9003-70-7.

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Ligand Exchange in Ferrocene with a η^1 Ligand: CO. A Bridge between Ferrocene and Cyclopentadienyl–Iron–Dicarbonyl Chemistry

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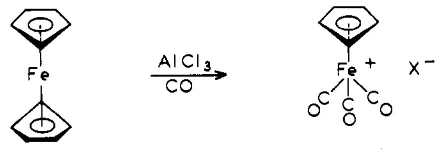
The plethora of ferrocene chemistry can be categorized into (i) reactions retaining the sandwich structure and (ii) complete decomplexation with use of drastic conditions.[1] The only ligand-exchange reactions known involve replacement of one[2] or both[3] cyclopentadienyl rings with arenes, a promising field with respect to activation and arene synthesis.[4] Yet this latter chemistry falls into the first of these two categories. We report here the first transformation of ferrocene to a nonsandwich organometallic compound, namely, its reaction with CO using $AlCl_3/H_2O$ to give $CpFe(CO)_3{}^{+}$ [5] (eq 1). Since this reaction proceeds cleanly in good yield, it opens a useful bridge between rich chemistries of both ferrocene[1] and "Fp".[6]



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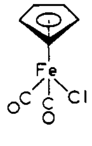
Experimental Section

Into a 500-mL steel autoclave were successively introduced 2.79 g of ferrocene (15 mmol), 0.81 g of aluminum powder (15 mmol), 0.27 g of water (15 mmol), and 40 mL of heptane. The mixture was flushed with N_2 and 6 g of $AlCl_3$ (45 mmol) was added under N_2. The autoclave was pressurized with 100 atm of CO, mechanically shaken, and heated to 120 °C for 12 h (CO pressure by now was 120 atm). The reaction mixture was then hydrolyzed at 0 °C with 100 mL of ice water and filtered, and the two phases were separated. The aqueous phase was washed twice with 100 mL of ether and then added to a filtered solution of $NaPF_6$ (20 mmol). The pale yellow precipitate was filtered, dried, and recrystallized from acetone. A 3.7-g yield of PF_6^- salt (70%) was isolated. η^5-$C_5H_5Fe(CO)_3{}^+PF_6{}^-$ [5] exhibited a single peak at $\delta = 6.18$ in the ^1H NMR spectrum (CD_3COCD_3) and peaks at ν_{CO} 2135 and 2072 cm^{-1} in the IR spectrum.[5] The organic layer was washed with $NaHCO_3$ and water and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on thick layer plates of silica with hexane as eluant. A 0.3-g yield of ferrocene, 0.05 g of **4**,[7] and 0.01 g of the mixture of **5**[7] and **6**[7] were isolated and identified by TLC, melting point, and ^1H NMR. See Table I for various experimental conditions. At 80 °C and 5 atm (no H_2O), 5% of **4**, 0.5% of **5** + **6**, 20% of **3**, and traces of **2** were formed (5% ferrocene was recovered).



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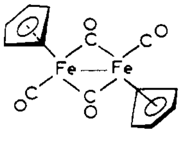

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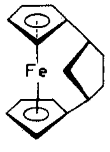

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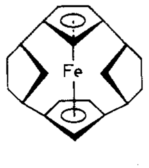

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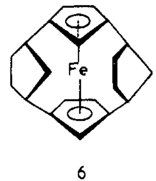

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