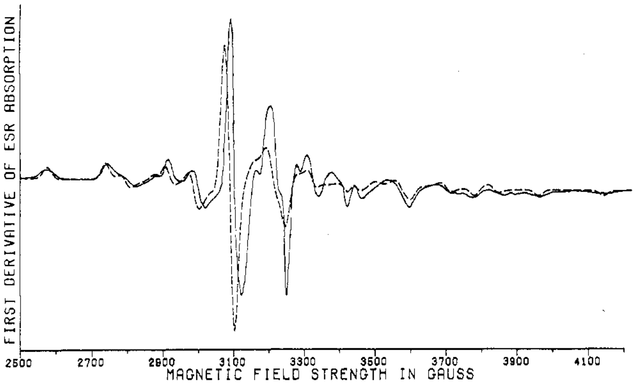

Figure 2. Experimental and simulated ESR spectra of copolymer-attached Cp_2NbCl_2.

Table I. Spin-Hamiltonian Parameters

	copolymer-attached		
	$\mathrm{CpNbCl_3}^a$	$\mathrm{Cp_2NbCl_2}^a$	$\mathrm{Cp_2NbCl_2}^b$
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.

References and Notes

(1) C. P. Stewart and A. L. Porte, *J. Chem. Soc. Dalton Trans.*, 722–9 (1973).
(2) C. P. Lau, Ph.D. Dissertation, Michigan State University, East Lansing, MI, 1977; J. G.-S. Lee and C. H. Brubaker, Jr., *J. Organomet. Chem.*, **135**, 333 (1977).
(3) R. H. Sands, *Phys. Rev.*, **99**, 1222–6 (1955).
(4) C. P. Stewart and A. L. Porte, *J. Chem. Soc., Dalton Trans.*, 1661–6 (1972).
(5) P. C. Taylor, J. F. Baugher, and H. M. Kriz, *Chem. Rev.*, **75**, 203–40 (1975).

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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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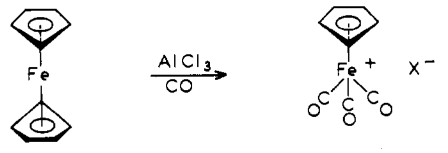
The plethora of ferrocene chemistry can be categorized into (i) reactions retaining the sandwich structure and (ii) complete decomplexation with use of drastic conditions.[1] The only ligand-exchange reactions known involve replacement of one[2] or both[3] cyclopentadienyl rings with arenes, a promising 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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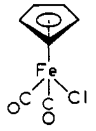
Experimental Section

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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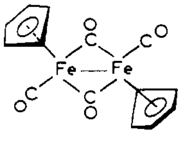

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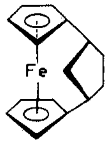

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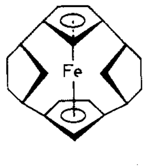

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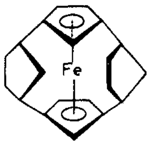

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Table I. Yields in Ligand Exchange between Ferrocene and CO with Different Reaction Conditions (12 h)

temp, °C	*P*(CO), atm	presence of H_2O	yield, %
80	5	no	10
80	100	no	20
80	100	yes	47
110	120	no	30
110	120	yes	70

Discussion

The lack of report of ligand exchange of a ferrocene ring with 2-electron ligands is related to the use of a Lewis acid necessary for the Cp cleavage. Therefore, only those 2-electron ligands which do not interact too strongly with $AlCl_3$ (e.g., CO) are valid candidates. From our mechanistic studies[2c] (aluminum chloride complexes either to the ring providing its cleavage or to the metal thus inhibiting the cleavage) it follows that water hydrolyzes the Fe–Lewis acid bond formed,[8] thus considerably assisting the ring cleavage. Therefore the best stoichiometry is ferrocene/$AlCl_3$/Al/H_2O = 1/3/1/1 (instead of anhydrous conditions: ferrocene/$AlCl_3$/Al = 1/2/1). After hydrolysis of the reaction mixture, η^5-$C_5H_5Fe(CO)_3{}^+Cl^-$ was the only organometallic product found in the aqueous phase; minor amounts of known[7] d^6 iron neutral complexes are isolated from the organic phase (see Experimental Section). Thus the simplicity of the reaction and the low cost of the reactants make eq 1 a very convenient route to **1** in comparison to the other known procedures[5]—a finding of interest because of the great number of Fp complexes accessible by nucleophilic attack of **1**.[9]

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Registry No. **2**, 12107-04-9; **3**, 32757-46-3; **4**, 12088-07-2; **5**, 59246-01-4; **6**, 60133-99-5; η^5-$C_5H_5Fe(CO)_3{}^+PF_6{}^-$, 38834-26-3; ferrocene, 102-54-5.

References and Notes

(1) M. Rosenblum, "Chemistry of the Iron Group Metallocenes", Part I, Wiley, New York, 1965.

(2) (a) A. N. Nesmeyanov, "Abstracts of the 3rd International Conference on Organometalic Chemistry", Butterworths, London, 1967; (b) A. N. Nesmeyanov, *Adv. Organomet. Chem.*, **10**, 1 (1972); (c) D. Astruc and R. Dabard, *J. Organomet. Chem.*, **96**, 283 (1975); **111**, 339 (1976); (d) E. Roman and D. Astruc, *Nouv. J. Chim.*, **1**, 183 (1976); (e) D. Astruc and R. Dabard, *Bull. Soc. Chim. Fr.*, 2571 (1975); (f) R. G. Sutherland, *Organomet. Chem. Libr.*, **3**, 311 (1977); (g) W. H. Morrison, E. Y. Ho, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **96**, 3603 (1974); *Inorg. Chem.*, **14**, 500 (1975); (h) P. Bachman and H. Singer, *Z. Naturforsch., B*, **31**, 525 (1976).

(3) (a) D. Astruc, *Tetrahedron Lett.*, 3437 (1973); (b) D. Astruc and R. Dabard, *Tetrahedron*, **32**, 245 (1976).

(4) (a) D. Astruc, E. Roman, J.-R. Hamon, and P. Batail, *J. Am. Chem. Soc.*, **101**, 2240 (1979); (b) M. F. Semmelhack, *Ann. N.Y. Acad. Sci.*, **295**, 36 (1977); (c) R. G. Sutherland, W. J. Pannekoek, and C. C. Lee, *ibid.*, **295**, 192 (1977).

(5) (a) A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 3172 (1971); (b) E. O. Fischer and K. Fichtel, *Chem. Ber.*, 1200 (1961); (c) R. K. Kochbar and R. Pettit, *J. Organomet. Chem.*, **6**, 272 (1966); (d) L. Busetto and R. Angelici, *Inorg. Chim. Acta*, **2**, 3 (1968); (e) W. F. Williams and F. J. Lawlor, *J. Chem. Soc., Chem. Commun.*, 1329 (1973); (f) E. C. Johnson, T. J. Meyer, and N. Winterton, *Inorg. Chem.*, **10**, 1673 (1971); (g) B. D. Dombek and R. J. Angelici, *Inorg. Chim. Acta*, **7**, 345 (1973); (h) J. A. Ferguson and T. J. Meyer, *Inorg. Chem.*, **10**, 1025 (1971).

(6) M. Rosenblum, *Acc. Chem. Res.*, **7**, 2087 (1975).

(7) (a) D. Astruc, R. Dabard, P. Batail, D. Grandjean, and M. L. Martin, *Tetrahedron Lett.*, 11, 829 (1976); (b) D. Astruc, P. Batail, and M. L. Martin, *J. Organomet. Chem.*, **113**, 77 (1975); (c) P. Batail, D. Grandjean, D. Astruc, and R. Dabard, *ibid.*, **102**, 79 (1975); **110**, 91 (1976).

(8) (a) A. N. Nesmeyanov, N. A. Vol'kenau, I. N. Bolesova, and L. S. Polovnikova, *Koord. Khim.*, **1**, 1252 (1975); (b) E. Roman and D. Astruc, *Inorg. Chim. Acta Lett.*, in press.

(9) L. Busetto and R. J. Angelici, *J. Am. Chem. Soc.*, **91**, 3197 (1969).