Acknowledgment. We thank Daniel F. Drummond for assistance with the mass spectral measurements and Paul D. Boyle for collecting the X-ray diffraction data for $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$. The Natural Sciences and Engineering Research Council of Canada, the University of New Brunswick Research Fund, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, are gratefully acknowledged for financial support.

Supplementary Material Available: Figures with numbering schemes and tables of hydrogen atom positions, anisotropic and isotropic thermal parameters, and comprehensive bond distances and angles for $[C_5Me_5O][(\eta\text{-}C_5Me_5)Mo_6O_{18}]$ and $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)(\mu\text{-}CO_3H)(\mu\text{-}O)$ and figures with numbering schemes and tables of crystal and refinement data, atomic positions, thermal parameters, and bond distances and angles for $[(\eta\text{-}C_5Me_5)MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$ (22 pages). Ordering information is given on any current masthead page.

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(48) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

Structure of the [1.1]Metallocenophanes of Fe and Ru: Single-Crystal X-ray Diffraction Analysis of $(C_5H_4\text{-}CH_2\text{-}C_5H_4)_2Fe_2$, $(C_5H_4\text{-}CH_2\text{-}C_5H_4)_2FeRu$, and $(C_5H_4\text{-}CH_2\text{-}C_5H_4)_2Ru_2$

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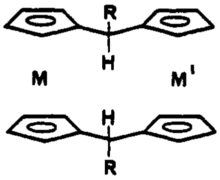
Single-crystal X-ray diffraction studies of the [1.1]metallocenophanes of Fe and Ru [(Cp-CH$_2$-Cp)$_2$MM′, 1, M = M′ = Fe; 2, M = Fe,M′ = Ru; and 3, M = M′ = Ru] clearly document that all three compounds exist only in a syn conformation which, in twisting by angles between 10° and 28°, can relieve the steric crowding of the inner α-Cp protons. The anti conformation, in which such strain relief is not possible because of structural rigidity, does not exist. The structures indicate the presence of two fully independent metallocenes in each of these systems and give no obvious indication of any metal–metal bonding: the metallocene halves show now sign of distortion, and the Cp rings in them are coplanar. However, the larger twist in [1.1]ruthenocenophane indicates a metal–metal interaction which, while leading to a net nonbonding situation for the Ru atoms, drastically lowers the redox potential of this compound. Crystal data: compounds 1–3 crystallize in the monoclinic space group $P2_1/c$ with $Z = 4$; (1) $C_{20}H_{20}Fe_2$, $a = 7.894$ (3) Å, $b = 10.530$ (3) Å, $c = 19.402$ (6) Å, $\beta = 94.57$ (3)°; (2) $C_{20}H_{20}FeRu$, $a = 7.980$ (2) Å, $b = 10.724$ (3) Å, $c = 19.112$ (5) Å, $\beta = 95.76$ (2)°; (3) $C_{20}H_{20}Ru_2$, $a = 6.003$ (3) Å, $b = 19.472$ (7) Å, $c = 14.196$ (5) Å, $\beta = 92.55$ (4)°.

Introduction

The [1.1]metallocenophanes 1–3 of Fe and Ru are an intensively studied trio. We here communicate the full structural characterization of the three parent systems. Although mention, without details, of the structures of 1 and 2 has already been made in a review of metallocenophanes,[3] it has only been possible to complete this series of structural investigations through an improvement[4] in the synthesis of 3.

Much interest has centered on the possible interactions between the two metals (a) in the neutral species, (b) in their monocations, and (c) in the dications or trications obtained by chemical or electrochemical means. One aim of this work has been to establish and use the structural information on the neutral compounds to provide a link to the differences in their redox properties, especially regarding metal–metal interactions which might facilitate the oxidation and lead to more stable oxidized species.



1: R = H, M = M′ = Fe
2: R = H, M = Fe, M′ = Ru
3: R = H, M = M′ = Ru
4: R = CH$_3$, M = M′ = Fe

Background Information: [1.1]Metallocenophanes

[1.1]Ferrocenophane (1) and Its Derivatives. Until we started the present work, the only structurally characterized [1.1]metallocenophanes were the bridge substituted exo,exo-1,12-dimethyl[1.1]ferrocenophane (4) and

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(3) Mueller-Westerhoff, U. T. *Angew. Chem.* **1986**, *98*, 700; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 702.

(4) Mueller-Westerhoff, U. T.; Swiegers, G. F. Submitted for publication.

the two 2,2′- and 3,3′-trimethylene[1,1]ferrocenophanes in which one of the ferrocene units is bridged by a three-carbon chain either next to (2,2′) or away from (3,3′) the bridging methylene groups. Compound 4 was shown to exist[5] in a syn conformation, twisted to eliminate the steric repulsion between the inner α-protons. The trimethylene derivatives do not allow such a twist, although the 3,3′-derivative is much more flexible than its 2,2′-counterpart. In these two cases the steric problem is resolved mainly by deformations of the two ferrocenes.[6]

Models show that the anti conformation is rigid and that it cannot relieve this steric strain. One example exists, however, in which a [1.1]metallocenophane prefers the anti conformation. This is the bis(di-*n*-butylstannyl)-bridged analog of 1, prepared and investigated by Seyferth and co-workers, in which the greater length of the C–Sn bonds, as compared to the C–C bonds in 1, reduces the steric repulsion of the inner ring protons and allows this unusual anti conformation to be attained.[7] For 1 no such relief exists, and we therefore would expect this compound to adopt the syn conformation.

Oxidation of 1 proceeds in two well-defined, reversible steps. Both are one-electron oxidations and clearly are centered first on one and then on the other of the ferrocene units. The monocation is stable and can be isolated. A single-crystal diffraction study of the triiodide salt of the monocation of the dimethyl derivative 4 has shown[8] it to be a localized mixed valence compound containing one ferrocene and one ferrocenium ion. No metal–metal interaction is evident in this cation. The dications of 1 and 4 are strong C–H acids and easily lose a proton from one of the bridges, forming carbenium ions, of which the BF_4 salt of the parent system has been studied by single-crystal X-ray diffraction.[9] So far, a structural characterization of the dication of 1 has not been attempted.

[1.1]Ruthenocenoferrocenophane (2). The oxidation of 2 is unique in that a mono- and a trication, but no dication is observed. This is due to the known nature of the oxidation of ferrocene (ca. 400 mV, reversible one-electron oxidation) and ruthenocene (920 mV, irreversible two-electron oxidation). The combination of a ferrocene and a ruthenocene in 2, leads to a low-potential formation of a monocation, followed by a high-potential oxidation to the trication. This speaks for negligible metal–metal interactions in 2, in which the two metallocenes hardly know of each other.

The structure of the mixed [1.1]metallocenophane (2) was thus expected to show two independent metallocenes, but it also should reflect the differences in ring–ring distance between ferrocene[10] (3.3 Å) and ruthenocene[11] (3.7 Å). The overall structure would still be that of a twisted, syn-oriented molecule.

[1.1]Ruthenocenophane (3). The chemical or electrochemical oxidation of 3 to the stable, diamagnetic dication 3^{2+} is surprisingly easy (reversible two-electron oxidation at 380 mV, ca. 540 mV below the potential of an isolated ruthenocene!).[12] The oxidation of Cp_2Ru has seen many different interpretations,[13-23] but it now is highly probable that under the usual cyclic voltammetry conditions a reactive dication is formed first, which then very rapidly binds to a neutral Cp_2Ru species to form the metal–metal-bonded dimer dication $Cp_4Ru_2^{2+}$. The electrochemical oxidation requires a potential of 920 mV vs SCE and, as would be expected from the above, is irreversible. Although this dimer structure has not been proven so far, the work by Taube and others on the oxidation of Cp_2Os makes it very plausible.[24] In this work, the dimer dication $Cp_4Os_2^{2+}$ was isolated and fully characterized. The X-ray crystal structure revealed it to have an Os–Os single bond of 3.04 Å. Taube also suggested that 3^{2+} should have a Ru–Ru single bond.[24] This has recently been confirmed by a crystallographic study on single crystals of the bis-BF_4 salt of 3^{2+} and reasons for the easy formation of a Ru–Ru single bond were given.[25]

Some form of metal–metal interactions in the neutral compound 3 would certainly explain the ease of oxidation, because it would predict a pathway to bypass the formation of a high-potential oxidation intermediate (a Cp_2Ru^{2+}–Cp_2Ru pair), which then would stabilize itself by forming a Ru–Ru bond. However, NMR and other data make the existence of any kind of Ru–Ru bond formation in 3 highly unlikely.

The structure of the parent compound 3 was therefore of special interest. Aside from proving or disproving the existence or absence of a Ru–Ru interaction, it was to be expected that a syn orientation of the bridges and a twist around the bridging carbons should be preferred.

Experimental Section

The [1.1]metallocenophanes 1–3 were synthesized according to published procedures.[3,4,26,27] The investigation of 3 was hampered by the lack of an efficient ruthenocene synthesis which would also be applicable to the preparation of this cyclic system. A recent improvement of ruthenocene syntheses through the use of bisruthenium(II) tetracarboxylates ($Ru_2(OCOR)_4$, $R = C_3H_7$ or C_7H_{15}) and CpNa held promise that this problem could be overcome.[4] However, the formation of oligomers at the expense of 3 again precluded a significant improvement in this preparative

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(5) McKechnie, J. S.; Maier, C. A.; Bersted, N.; Paul, I. C. *J. Chem. Soc., Perkin Trans.* **1973**, *2*, 138.

(6) Singletary, N. J.; Hillman, M.; Dauplaise, H.; Kvick, Å.; Kerber, R. C. *Organometallics* **1984**, *3*, 1427.

(7) Clearfield, A.; Simmons, C. J.; Winters, H. P., Jr.; Seyferth, D. *Inorg. Chim. Acta* **1983**, *75*, 139.

(8) Moore, M. F.; Wilson, S. R.; Hendrickson, D. N.; Mueller-Westerhoff, U. T. *Inorg. Chem.* **1984**, *23*, 2918.

(9) Mueller-Westerhoff, U. T.; Nazzal, A.; Pröasdorf, W.; Mayerle, J. J.; Collins, R. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 293.

(10) Seiler, P.; Dunitz, J. D. *Acta Crystallogr.* **1979**, *B35*, 1074.

(11) Hardgrove, G. L.; Templeton, D. H. *Acta Crystallogr.* **1959**, *12*, 28.

(12) Diaz, A.; Mueller-Westerhoff, U. T.; Nazzal, A.; Tanner, M. *J. Organomet. Chem.* **1982**, *236*, C45.

(13) Wilkinson, G. *J. Am. Chem. Soc.* **1952**, *74*, 6146.

(14) Sohn, Y. S.; Schlueter, A. W.; Hendrickson, D. N.; Gray, H. B. *Inorg. Chem.* **1974**, *13*, 301.

(15) Savitskii, A. V.; Syrkin, Y. K. *Tr. Khim. Khim. Technol.* **1961**, *4*, 165.

(16) Bublitz, D. E.; Hoh, G.; Kuwana, T. *Chem. Ind. (London)* **1959**, 653.

(17) Kuwana, T.; Bublitz, D. E.; Hoh, G. *J. Am. Chem. Soc.* **1960**, *62*, 5811.

(18) Gubin, S. P.; Smirnova, S. A.; Denisovich, L. I.; Lubovich, A. A. *J. Organomet. Chem.* **1971**, *30*, 243.

(19) Hendrickson, D. N.; Sohn, Y. S.; Morrison, W. H., Jr.; Gray, H. B. *Inorg. Chem.* **1972**, *11*, 808.

(20) Nesmeyanov, A. N.; Lubovich, A. A.; Yurêva, L. P.; Gubin, S. P.; Perevalova, E. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 935.

(21) Borrell, P.; Henderson, E. *J. Chem. Soc., Dalton Trans.* **1975**, 432.

(22) Smirnova, S. A.; Gubin, S. P.; Lubovich, A. A.; Denisovich, L. I. *Dokl. Akad. Nauk SSSR* **1971**, *200*, 605.

(23) Hill, M. G.; Lamanna, W. M.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 4690.

(24) Droege, M. W.; Harman, W. D.; Taube, H. *Inorg. Chem.* **1987**, *26*, 1309.

(25) Mueller-Westerhoff, U. T.; Rheingold, A. L.; Swiegers, G. F. *Angew. Chem.*, accepted for publication. The dication 3^{2+} has a Ru–Ru bond, the length of which (2.953 (1) Å) qualifies it as a single bond. The twisting of the two metallocene halves reaches an angle of 75°, and the Cp ligands of each ruthenocene deviate from coplanarity by 28° (average centroid–Ru–centroid angle 152°).

(26) Cassens, A.; Eilbracht, P.; Nazzal, A.; Prössdorf, W.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1981**, *103*, 6367.

(27) Mueller-Westerhoff, U. T.; Nazzal, A.; Tanner, M. *J. Organomet. Chem.* **1982**, *236*, C41.

Table I. Summary of Crystallographic Data for 1–3

	1	2	3
	(a) Crystal Parameters		
formula	$C_{22}H_{20}Fe_2$	$C_{22}H_{20}FeRu$	$C_{22}H_{20}Ru_2$
formula wt	405.17	441.32	486.54
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	7.894 (3)	7.980 (2)	6.003 (3)
b, Å	10.530 (3)	10.724 (3)	19.472 (7)
c, Å	19.402 (6)	19.122 (5)	14.296 (5)
β, deg	94.57 (3)	95.76 (2)	92.55 (4)
V, Å^3	1607.6 (9)	1618.4 (7)	1658 (1)
Z	4	4	4
ρ(calc), g cm^{-3}	1.674	1.811	1.949
cryst size, mm	0.19 × 0.19 × 0.22	0.10 × 0.25 × 0.30	0.32 × 0.40 × 0.40
color	orange	orange	colorless
μ, cm^{-1}	18.03	18.11	17.88
	(b) Data Collection		
diffractometer	Nicolet R3m		
radiation	Mo Kα (λ = 0.710 73 Å)		
scan limits	4–50	4–48	4–50
rflns collected	3105	2582	3140
obsvd indpt rflns $F_o \geq 3\sigma(F_o)$	2163	2202	2234
max, min transms	0.774/0.716	0.558/0.461	0.299/0.117
decay, %	<1	<1	~3
	(c) Refinement		
$R(F)$, $R(wF)$	0.0464, 0.0432	0.0419, 0.0457	0.0474, 0.0577
GOF	1.72	1.82	1.26
$\Delta(\rho)$ max, eÅ^{-3}	0.43	0.95	1.57
N_o/N_v	7.26	9.41	9.59

approach. Nevertheless, we were able to obtain sufficient quantities of 3 to grow single crystals. In all three cases, purification by column chromatography (40–200 mesh silica gel, CCl_4) was followed by recrystallization from heptane or hexane.

Crystal Growth. A sample of 1 was dissolved in a large volume of hexane at room temperature in an argon atmosphere. The flask was closed with a serum cap and a small hole was punched into the septum. The solution was left standing in the dark for 3 months. After this time, most of the hexane had evaporated and several well-formed crystals were found together with some leaflike smaller crystals. The finer material was slurried up and decanted. The large crystals were suspended in cold hexane and isolated by filtration.

Single crystals of 2 were obtained as orange needles by slow cooling of a heptane solution under an atmosphere of N_2.

Ruthenocenophane (3) was dissolved in an excess of degassed hexane. The solution was filtered into a round-bottomed flask which was then closed with a clump of cotton. A syringe needle was connected to a N_2 line and inserted through the cotton plug. A gentle stream of N_2 was maintained for several days, during which time colorless crystals of 3 formed at the walls of the flask and in the remaining solution. When 90% of the solvent had evaporated, the mixture was filtered under nitrogen, the crystals were washed briefly with cold hexane and dried in a stream of nitrogen. The product was transferred to nitrogen-flushed vials and sealed tightly.

X-ray Crystal Structure Determinations. The crystallographic data for the structures of 1–3 are collected in Table I. Preliminary photographic data indicated $2/m$ Laue symmetry for the three structures; the space groups were unambiguously assigned from systematic absences. Empirical absorption corrections were applied to the data sets. The structures of 1 and 2 are isomorphous. For 2, the metal–atom thermal parameters showed no evidence of substantial Fe/Ru disorder. The structures of 1 and 3 were solved by direct methods, and refinement of 2 was initialized from the coordinates of 1.

All non-hydrogen atoms were anisotropically refined. The ring hydrogen atoms were treated as idealized isotropic contributions, whereas the methylene-bridge hydrogen atoms were located and isotropically refined. Atomic coordinates for 1, 2, and 3 are given in Tables II, III, and IV, respectively. Selected bond distances and angles are summarized in Table V. All computations used the SHELXTL 5.1 program library (G. Sheldrick, Nicolet (Siemens), Madison, WI).

Table II. Atomic Coordinates (10^4) and Isotropic Thermal Parameters (Å × 10^3) with Esd's in Parentheses for the Non-Hydrogen Atoms in 1

atom	x	y	z	U^a
Fe(1)	1201 (1)	1036 (1)	1333 (1)	32 (1)
Fe(2)	3513 (1)	926 (1)	3705 (1)	35 (1)
C(1)	1772 (5)	2997 (4)	2614 (2)	36 (1)
C(2)	4894 (5)	664 (4)	2185 (2)	36 (1)
C(11)	745 (5)	2506 (4)	1990 (2)	34 (1)
C(12)	953 (5)	2963 (4)	1308 (2)	38 (1)
C(13)	−277 (6)	2398 (4)	840 (2)	45 (2)
C(14)	−1305 (5)	1590 (4)	1221 (2)	44 (1)
C(15)	−665 (5)	1664 (4)	1931 (2)	38 (1)
C(16)	3498 (5)	226 (4)	1660 (2)	33 (1)
C(17)	3473 (5)	608 (4)	954 (2)	39 (1)
C(18)	2139 (5)	−24 (4)	574 (2)	48 (2)
C(19)	1316 (5)	−830 (4)	1029 (2)	43 (1)
C(20)	2153 (5)	−656 (4)	1703 (2)	40 (1)
C(21)	1861 (5)	2289 (4)	3292 (2)	33 (1)
C(22)	2844 (5)	2749 (4)	3895 (2)	43 (1)
C(23)	2533 (6)	1961 (4)	4464 (2)	53 (2)
C(24)	1383 (6)	1016 (4)	4225 (2)	50 (2)
C(25)	958 (5)	1196 (4)	3504 (2)	40 (1)
C(26)	4914 (5)	302 (4)	2932 (2)	37 (1)
C(27)	5974 (5)	935 (4)	3464 (2)	48 (2)
C(28)	5817 (6)	292 (5)	4093 (3)	55 (2)
C(29)	4693 (6)	−764 (4)	3968 (2)	53 (2)
C(30)	4164 (6)	−745 (4)	3254 (2)	42 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Atomic Coordinates (10^4) and Isotropic Thermal Parameters (Å × 10^3) with Esd's in Parentheses for the Non-Hydrogen Atoms in 2

atom	x	y	z	U^a
Ru	1125 (1)	1136 (1)	1294 (1)	31 (1)
Fe	3587 (1)	1070 (1)	3691 (1)	26 (1)
C(1)	1745 (7)	3148 (5)	2606 (3)	33 (2)
C(2)	4936 (7)	751 (6)	2143 (3)	31 (2)
C(11)	680 (6)	2704 (5)	1968 (3)	29 (2)
C(12)	−776 (6)	1911 (6)	1905 (3)	36 (2)
C(13)	−1430 (7)	1844 (6)	1188 (3)	39 (2)
C(14)	−394 (7)	2612 (6)	794 (3)	41 (2)
C(15)	881 (7)	3147 (5)	1275 (3)	37 (2)
C(16)	3515 (7)	268 (5)	1631 (3)	30 (2)
C(17)	2200 (7)	−589 (5)	1712 (3)	37 (2)
C(18)	1334 (8)	−808 (6)	1033 (4)	49 (2)
C(19)	2086 (8)	−93 (6)	538 (3)	45 (2)
C(20)	3433 (7)	552 (5)	896 (3)	36 (2)
C(21)	1865 (7)	2396 (5)	3275 (3)	31 (2)
C(22)	2798 (7)	2836 (6)	3903 (3)	40 (2)
C(23)	2509 (8)	2024 (6)	4460 (3)	47 (2)
C(24)	1415 (8)	1059 (6)	4180 (3)	45 (2)
C(25)	1035 (7)	1292 (5)	3458 (3)	35 (2)
C(26)	5004 (7)	451 (6)	2910 (3)	35 (2)
C(27)	6035 (8)	1172 (7)	3429 (3)	49 (2)
C(28)	5955 (8)	549 (8)	4089 (3)	63 (3)
C(29)	4951 (9)	−499 (7)	3979 (4)	57 (3)
C(30)	4356 (8)	−584 (6)	3264 (3)	40 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results

[1.1]Ferrocenophane (1). The growth of high quality single crystals of 1 is extremely difficult and capricious, because this compound tends to form very thin leaflets. After being frustrated by a number of failed attempts to grow useful single crystals, we eventually succeeded, by pure serendipity, in obtaining large crystals in an unexpectedly simple manner by very slow evaporation of a heptane solution of 1 under argon during several months. An aggregate of single crystals was cleaved to produce the sample crystal for this study.

Table IV. Atomic Coordinates (10^4) and Isotropic Thermal Parameters (Å × 10^3) with Esd's in Parentheses for the Non-Hydrogen Atoms in 3

	x	*y*	*z*	U^a
Ru(1)	3995.9 (9)	1358.0 (3)	6797.9 (3)	36.4 (2)
Ru(2)	4276.3 (9)	3770.3 (3)	6765.8 (4)	37.8 (2)
C(1)	5969 (13)	2546 (3)	5331 (5)	44 (2)
C(2)	6432 (13)	2533 (4)	8178 (5)	46 (3)
C(11)	5178 (11)	1823 (4)	5512 (4)	40 (2)
C(12)	3032 (12)	1523 (3)	5317 (4)	43 (2)
C(13)	3154 (14)	813 (4)	5487 (5)	55 (3)
C(14)	5371 (13)	647 (4)	5776 (5)	57 (3)
C(15)	6632 (13)	1280 (4)	5791 (5)	48 (3)
C(16)	4649 (11)	1980 (3)	8061 (4)	37 (2)
C(17)	2366 (11)	2024 (4)	7790 (4)	41 (2)
C(18)	1426 (13)	1365 (4)	7831 (5)	52 (3)
C(19)	3116 (14)	892 (4)	9127 (5)	55 (3)
C(20)	5103 (13)	1274 (4)	8273 (4)	46 (2)
C(21)	4427 (11)	3138 (3)	5485 (4)	37 (2)
C(22)	5009 (12)	3830 (3)	5290 (2)	44 (2)
C(23)	3140 (12)	4259 (4)	5440 (5)	52 (3)
C(24)	1421 (12)	3849 (4)	5766 (5)	48 (2)
C(25)	2159 (11)	3154 (4)	5789 (4)	43 (2)
C(26)	5736 (12)	3276 (4)	8026 (4)	43 (2)
C(27)	7238 (13)	3780 (4)	7717 (5)	55 (3)
C(28)	6145 (15)	4430 (4)	7755 (5)	69 (3)
C(29)	3996 (16)	4332 (4)	8903 (5)	67 (3)
C(30)	3751 (13)	3621 (4)	8262 (4)	47 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Selected Bond Parameters for 1, 2, and 3

	1 (Fe/Fe)	2 (Fe/Ru)	3 (Ru/Ru)
(a) Bond Distances (Å)			
M···M	4.816 (2)	4.792 (2)	4.701 (1)
Fe–CNT(av)	1.647 (6)	1.665 (7)	
Ru–CNT(av)		1.788 (5)	1.819 (4)
Fe–C(av)	2.043 (4)	2.055 (6)	
Fe–C(range)	2.03–2.06	2.04–2.07	
Ru–C(av)		2.151 (6)	2.187 (7)
Ru–C(range)		2.15–2.17	2.16–2.20
(b) Bond Angles (deg)			
C(11)–C(1)–C(21)	121.3 (3)	120.4 (5)	119.4 (6)
C(16)–C(2)–C(26)	121.7 (3)	120.7 (5)	118.1 (6)
H(1a)–C(1)–H(1b)	103 (3)	101 (5)	107 (6)
H(2a)–C(2)–H(2b)	104 (3)	104 (4)	111 (6)
(c) Interplanar Angles (deg)			
[C(11)–C(15)]–[C(16)–C(20)]	2.4	2.0	0.6
[C(11)–C(15)]–[C(21)–C(25)]	13.8	18.6	32.7
[C(21)–C(25)]–[C(26)–C(30)]	1.4	1.8	1.6
[C(16)–C(20]–[C(26)–C(30)]	12.7	16.7	34.0

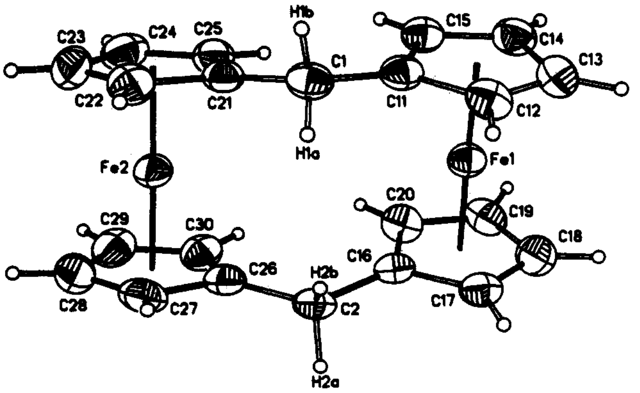

Figure 1. Molecular structure of [1.1]ferrocenophane (1) drawn with 40% probability thermal ellipsoids and arbitrary radius hydrogen atoms.

Crystallographic data for 1 are collected in Table II. The compound crystallizes as independent molecules shown in Figure 1, without any significant intermolecular contacts. The unit-cell packing diagram, Figure 2, shows that the molecules of 1 form weakly associated layers which are kept separated by the repulsive interaction of ring C–H groups. This layer structure very likely accounts for the tendency of 1, under most circumstances, to form thin platelets. Within the layers, the long molecular axes (parallel to the Fe–Fe vector) are aligned along the *c* axis, but they alternate perpendicularly. For this reason, C–H groups point directly toward the π-electron clouds of adjacent cyclopentadienyl rings; this attractive interaction is facilitated by the syn conformation of the metallocenophane.

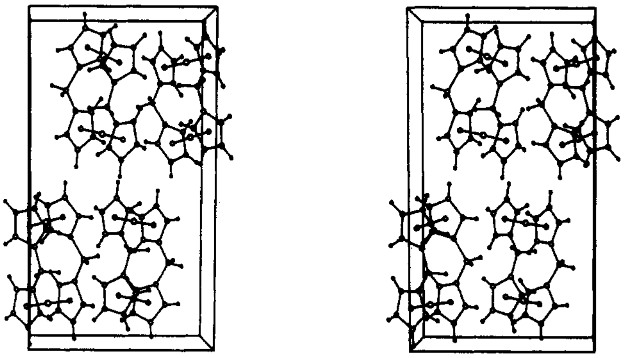

Figure 2. Stereoview of the unit-cell packing diagram for 1 as viewed down the *a* axis. The packing for the isomorphous 2 is similar.

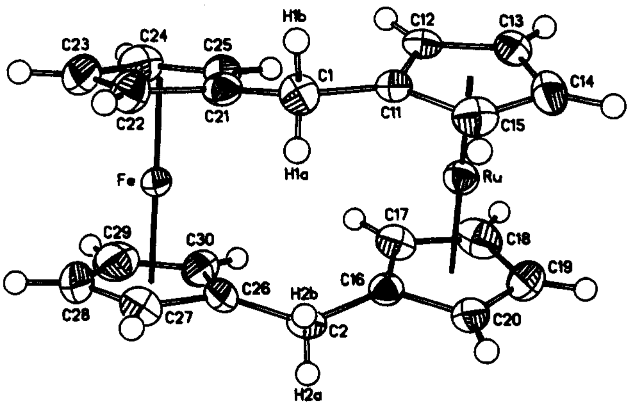

Figure 3. Molecular structure of the [1.1]ferrocenoruthenocenophane (2) drawn as in Figure 1.

As expected, the ferrocenophane structure showed great similarity with the published one of the dimethyl derivative 4. The CH_2-bridged Cp rings are twisted by 13.3° (av) with respect to each other. This movement, as can be very well observed when using Dreiding models, increases the distance between the CH_2 bridges, reduces the repulsion between the inner α-hydrogens, and brings them into a position where they are beyond van der Waals distances from each other. The Cp rings of each ferrocene unit are essentially coplanar. The Fe atoms are located symmetrically between the rings with Fe–C distance between 2.026 (4) and 2.058 (4) Å. This structure results in a Fe–Fe distances of 4.816 (2) Å. There is no indication whatsoever of any Fe–Fe interaction, be it attractive or repulsive.

[1.1]Ruthenocenoferrocenophane (2). On the basis of the structure of 1 and the evident independence of the ferrocene and ruthenocene halves of this molecule, as seen in the CV data, a structure was expected which would show undistorted metallocenes, unless the discrepancy of ring–ring distances between Cp_2Fe and Cp_2Ru would impose a deviation from Cp–ring coplanarity in the two constituent metallocenes.

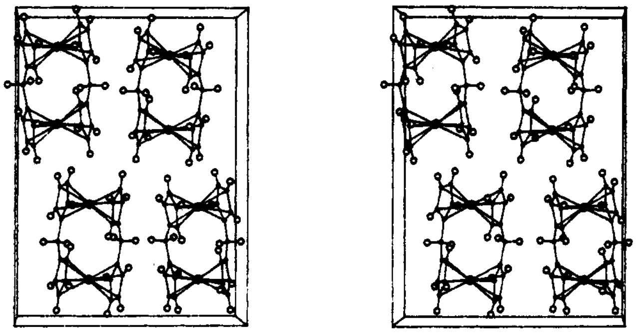

Figure 4. Stereoview of the unit-cell packing diagram for 3 as viewed down the *a* axis.

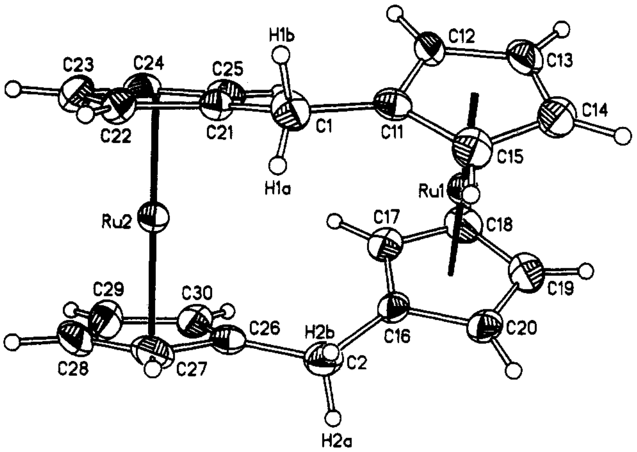

Figure 5. Molecular structure of the [1.1]ruthenocenophane (2) drawn as in Figure 1.

Single crystals of 2 were obtained as orange needles by very slow cooling of a heptane solution. The crystals are isomorphous with 1, and this offered the opportunity for disorder in the location of the metal atoms. However, the thermal parameters for Fe and Ru showed no evidence for a significant scrambling of identities, and the metal–atom environments appear normal for each metal (Table III).

The molecular structure is shown in Figure 3. The average Fe–centroid distance in 2 is 1.667 (7) Å, the Ru–centroid distance is 1.788 (5) Å; this compares with the respective values of 1.647 (6) Å in 1 and 1.819 (5) Å in 3. Clearly, the metal–atom environments in 2 are both within the extremes of the homometallic analogues, and the deviations are the result of distortions caused by the need to accomodate two differently sized metal atoms. Correspondingly, the average twist angle has increased from 13.3° in 1 to 17.7° in 2, which also brings with it a slight decrease in the Fe–Ru stance to 4.792 (2). The coplanarity of the Cp rings in each of the metallocenes is not affected. (Fe–C distances vary only between 2.045–2.075 Å; Ru–C distances are 2.150–2.166 Å.)

[1.1]Ruthenocenophane (3). Due to the ease with which 3 is oxidized to its dication, single-crystal growth had to be performed in an inert atmosphere. Slow evaportion over several days of a hexane solution of 3 in a gentle stream of nitrogen produced single crystals as colorless needles. They were stored under N_2 until the X-ray diffraction experiment was started. Deterioration during data collection was slow enough (3% decay, as given in Table I) to not significantly reduce the accuracy of the data (Table IV).

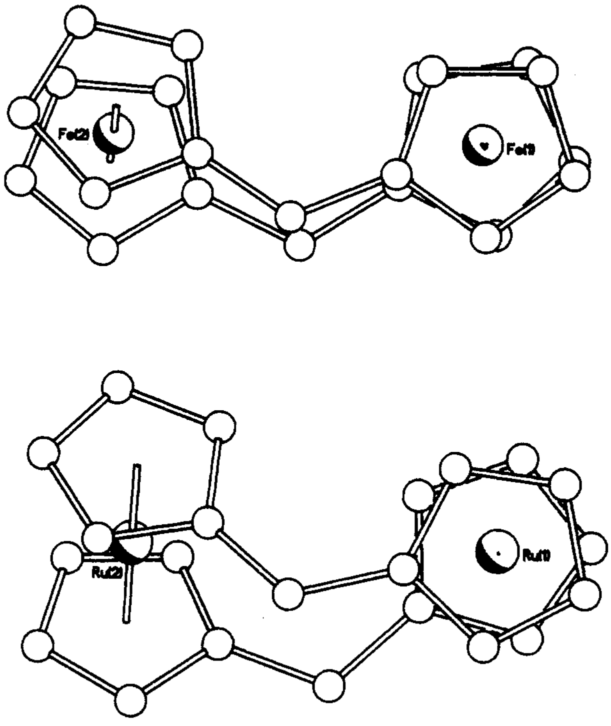

Figure 6. Comparison of the ring twisting in 1 and 3.

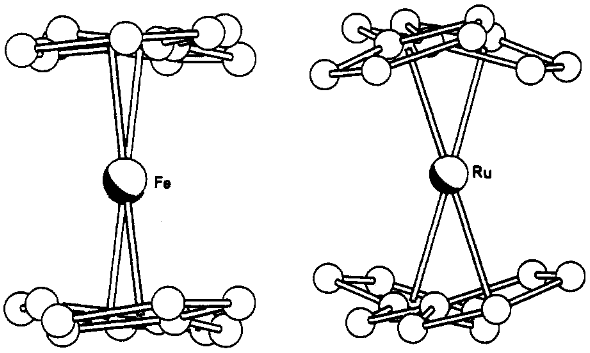

Figure 7. Side views of 1 and 3 showing the different twist angles.

The crystals of 3 are *not* isomorphous with 1 and 2, but, as in the other two cases, 3 also crystallizes without close intermolecular contacts. The unit-cell packing is shown in Figure 4. The molecules are aligned along the *b* axis in layers with weak interlayer interactions, similar to 1 and 2. However, within each layer, the Cp rings are more nearly face-to-face, rather than perpendicular, as found in 1 and 2. This probably results in a decrease in the intermolecular attractions within the layers (which led to laminar crystal growth in 1 and 2) and in emphasizing the attractive inter-layer interactions. This, in turn, may lead to the observed preference of crystals of 3 to form needles.

The molecular structure of 3 (Figure 5) shows a much stronger twisting than seen in either 1 or 2. In contrast to 1 and 2, in which the Cp rings are essentially eclipsed, the Cp rings in 3 are more nearly staggered. The difference is best represented by the average inter-ring angles between carbon atoms (0° for perfectly eclipsed and 36° for perfectly staggered Cp rings in a metallocene), which is approximately 10° in 1, 13° in 2, and 28° in 3. Correspondingly, the twist angle (av 33.4°) has increased greatly compared to 1 (13.3°) and 2 (17.7°), as shown in Figure 6 for 1 and 3. The metal–metal distance also is affected by this twist and is shortened to 4.701 (1) Å.

It is important to emphasize that this shortening is directly linked to the twisting of the molecule. Without additional information, it would not be possible to decide whether Ru–Ru interactions or packing forces are responsible for this twist in excess of what it needed to alleviate the repulsion between the inner α-protons. A bonding Ru–Ru interaction is unlikely, because the two ruthenocenes are perfectly symmetrical and there is no indication at all for any deviation from coplanarity or slippage of the rings to allow for a closer approach of the metals: all metal–carbon distances (Ru–C = 2.174–2.201 Å) are within the reported estimated standard deviations.

Discussion

Comparison of the Three Structures. The facility with which they can undergo conformational changes is a unique feature of all three [1.1]metallocenophanes and represents the motion of the CH_2 groups from one syn conformation to their mirror image coupled with a 36° rotational motion of the rings. The latter involves a (hard to visualize, unless a Dreiding model is at hand) movement of the ring carbon (and hydrogen) atoms from one nearly eclipsed to the nearest-neighbor eclipsed configuration and back to the original one. In this process all protons trade places: the exo bridge protons become the endo protons (and vice versa), the inner α-protons become the outer ones, and, similarly, the β-protons trade places. In solution, this movement is very rapid, so that, for example, the ^1H NMR spectra become very simple: one sharp singlet for all four bridge protons, and one multiplet each (four, in the case of 2, which contains two different metallocenes) for the α- and β-protons. In the solid state, we see that no such motion exists, but that the ability to twist has been used to find the lowest energy structure for the molecular crystals.

The low activation barrier of this movement is reflected in the crystal structure of 1–3. Some twisting must occur to relieve the repulsion of the inner α-protons of a completely coplanar structure. Where other factors become important, this repulsion can also be relieved by widening the $C–CH_2–C$ angle of the bridges. This was observed in the bridge carbenium ion of 1. In this case, the Fe–C interaction between both iron atoms and the sp^2-hybridized carbenium carbon atom pulls the bridge toward the center of the molecular ion and the bond angle at the CH_2 bridge widens accordingly.[9]

In the [1.1]metallocenophanes themselves, a simple twist can fully relieve all steric problem. That the molecules 1–3 do this to a different extent in the crystal, initially appears to be a consequence of the different intermolecular interactions rather than of intramolecular effects. In support of this, we could argue that all three metallocenophanes contain perfectly symmetrical and unperturbed metallocene subunits with average centroid–metal–centroid angles of 178.1° in 1 and 2 and an even smaller deviation (average 178.9) in 3, and that the differences in the twist angles seemingly do not influence the three molecules in any significant way. However, this would, as we will see below, be the wrong conclusion, because this twist has significant consequences for the redox behavior of 3.

The average distances between the metals and the ring carbon atoms in 1 (2.043 Å) and 3 (2.187 Å) are very close to those found for ferrocene[10] (2.033 Å) and ruthenocene[11] (2.186 Å). A small, but significant deviation is seen in 2, in which the ferrocene unit has expanded slightly (to a $r_{Fe–C}$ value of 2.055 Å) and the rutheocene has contracted ($r_{Fe–C}$ = 2.151 Å). Although the effect is small, it contributes to a reduction in dissymmetry induced on this compound by the two different metallocenes.

The most important obervation in these structures is the much larger twist angle in 3 as compared with those in 1 and 2 and the fact that 3 shows a distinctly shorter metal–metal distance. The overall structures seems to substantiate that metal–metal interactions do not exist in any of these compounds, and the metal–metal distances, which presumably are dictated by the ligands in all three compounds, are beyond normally accepted values for metal–metal interactions.

Special Features in [1.1]Ruthenocenophane (3). Since 3 very readily is oxidized to a dication, and since this dication was shown to contain a Ru–Ru single bond,[25] it is particularly significant that the metal–metal distance in 3 is definitely shortened and that this must relate to the facile oxidation and subsequent Ru–Ru bond formation. In 1 and 2 we find two fully independent oxidation potentials for the respective metallocenes, which shows that there is no direct interaction between them. However, both ruthenocenes in 3 are oxidized at the same time to form the dication.

Because the ruthenium d orbitals extend much further than those of iron, an interaction between two filled 4d orbitals along the Ru–Ru axis of 3 must be considered.[28] In the simplest approach (complete neglect of overlap), this interaction leads to a splitting of these two levels into a bonding and an antibonding one, resulting in a net bond order $p = 0$. An oxidant will remove an electron from the antibonding level, which increases the bond order to $p = 0.5$ and thereby enhances the Ru–Ru interaction and the splitting. A second ionization from the now strongly antibonding orbital will occur below the initial potential, and the process becomes a two-electron oxidation, which results in a Ru–Ru single bond ($p = 1.0$). This picture agrees with the structure and the reactivity of 3: the proximity of the ruthenium atoms does lead to a metal–metal interaction but no metal–metal bond. It also agrees with the structure of 3^{2+}: the dication possesses[25] a Ru–Ru single bond.

A more sophisticated approach, one which explicitly considers the function of the overlap integrals, would predict a net repulsive interaction,[29] because the antibonding orbital is destabilized more than the bonding one is stabilized.[30] In that case, we would expect to see an increase in the Ru–Ru distance rather than the observed decrease, which would be a fatal flaw in our argument. However, at an internuclear distance of 4.7 Å (the experimentally found Ru–Ru distance), the overlap integrals will be vanishingly small. Their complete neglect[29] ($S = 0$) is justified and validates the above simpler approach.

The not immediately obvious larger twisting of 3 is the key element for the drastic change in the redox behavior. In solution, this twist is part of the syn–syn exchange movement, and we can see from Dreiding models that the transition state for this process has an even shorter Ru–Ru distance, estimated from the models to be close to 3.6 Å, which must increase the splitting of the above two filled d levels and thus reduces the oxidation potential even further. Although the solution structures of these molecular acrobats do not necessarily have to be similar to what we have seen in the solid state, the fact that we find this twist and the associated shortening of the Ru–Ru distance in the crystal of 3 but not of 1 and 2 strongly supports our arguments relating to the unusual oxidation and reduction potentials and explains the nature of the

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(28) Similar interpretations have been invoked in photochemical oxidations in binuclear complexes of Pt and Ir. For some related interpretation, see: Smith, D. C.; Miskowski, V. M.; Mason, W. R.; Gray, H. B. *J. Am. Chem. Soc.* 1990, *112*, 3759.

(29) We thank a referee for reminding us that inclusion of overlap would present a problem for our interpretation.

(30) This is a consequence of the wave function normalization factor $N_i = 1/(2 \pm 2S)^{1/2}$ for a two-center problem ($i = 1, 2$) where S is the overlap integral. For $S = 0$ (neglect of overlap), $N_i = \pm\sqrt{2}$. For non-zero values of S, N_i and with it the energies of the resulting MO's are inequivalent.

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two-electron process of this compound.

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Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates for 1, 2, and 3 (19 pages). Ordering information is given on any current masthead page.

OM920286J

Synthesis, Structure, and Reactivity Properties of (η^5-C_5H_5)Ru[(C_2F_5)$_2$PCH_2CH_2P(C_2F_5)$_2$]X Complexes: New Electrophilic Analogues to (η^5-C_5H_5)Ru(CO)$_2$X Systems

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The synthesis, structure, and reactivity properties of CpRu(dfepe)Cl (1, dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$) are reported. Thermolysis of CpRu$(Ph_3P)_2$Cl in hydrocarbon solvent with excess dfepe at 140 °C gives 1 in good yield. In contrast to donor phosphine analogues, the chloride ligand in 1 is not labilized by halide-abstracting agents in the absence of trapping ligands. Crystallographic data for 1 confirm the presence of a short Ru–Cl bond (2.406 (1) Å). Sodium naphthylide reduction of 1 produces the thermally stable anion, Na^+[CpRu(dfepe)]$^-$, which upon treatment with $NH_4^+PF_6^-$ or CH_3I affords the corresponding hydride and methyl derivatives CpRu(dfepe)H (3) and CpRu(dfepe)Me (4) in moderate yield. The hydride complex 3 is more conveniently prepared by the reaction of 1 with $AgBF_4$ under 1 atm of H_2, presumably via the incipient formation of a highly acidic dihydrogen or dihydride cationic complex. Crystal data for 1: monoclinic, $P2_1/n$, with $a = 7.7709$ (15) Å, $b = 14.224$ (2) Å, $c = 20.814$ (4) Å, $\beta = 91.670$ (15)°, $V = 2299.6$ (7) Å^3, $Z = 4$, $R_F = 5.21\%$, and $R_{wF} = 7.21\%$.

Introduction

Piano-stool complexes (π-C_nR_m)M(L)$_x$ are an important class of organometallic compounds which continue to be the subject of numerous theoretical[1] and chemical investigations.[2,3] In the group VIII triad, ruthenium complexes of the general formulas CpRu(L)$_2$X and [CpRu(L)$_3$]$^+$ (L = R_3P or CO) have been studied extensively.[4] Electron-rich donor phosphine complexes CpRu$(R_3P)_2$X are typified by CpRu$(Ph_3P)_2$Cl, which provides a versatile entry into a wide variety of substitutional derivatives derived from either phosphine or chloride displacement under mild conditions.[4-6] The chemistry of electron-poor dicarbonyls CpRu(CO)$_2$X is likewise extensive yet often exhibits distinctly different reactivity patterns.[4]

We have reported the synthesis and properties of perfluoroalkylphosphine molybdenum π-arene complexes (η^6-C_6H_5R)Mo(dfepe)(L) (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$, L = N_2, CO, py, etc.) which serve as unique electron-poor analogues to unaccessed (π-arene)Mo(CO)$_2$(L) systems.[7] In light of the unusual steric and electronic properties of these Mo(0) arene piano stools, we have recently begun to examine the properties of potentially more electrophilic isoelectronic Mn(I)[8] and Ru(II) complexes. In this paper we present our initial studies of CpRu(dfepe)X systems and compare observed chemical properties with established CpRu(L)$_2$X and [CpRu(L)$_3$]$^+$ systems.

Results and Discussion

Synthesis and Structure of CpRu(dfepe)Cl (1). The ease of phosphine substitution previously demonstrated for CpRu$(Ph_3P)_2$Cl[5] suggested the straightforward synthesis of CpRu(dfepe)Cl (1) following eq 1. Although prior

$$\mathrm{CpRu(Ph_3P)_2Cl} \xrightarrow[\Delta]{\mathrm{dfepe}} \underset{1}{\mathrm{CpRu(dfepe)Cl}} + 2\mathrm{Ph_3P} \qquad (1)$$

studies with dfepe have shown it to be a very weak donor ligand, the complete displacement of both triphenylphosphine ligands from CpRu$(Ph_3P)_2$Cl can be achieved

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(1) (a) Kubacek, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180. (b) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (c) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536. (d) Poli, R. *Organometallics* **1990**, *9*, 1892.

(2) (a) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499. (b) Caulton, K. G. *Coord. Chem. Rev.* **1981**, *38*, 1. (c) Barnett, K. W.; Slocum, D. W. *J. Organomet. Chem.* **1972**, *44*, 1.

(3) Ernst, M. F.; Roddick, D. M. *Inorg. Chem.* **1990**, *29*, 3627, and references therein.

(4) (a) Bennett, M. A.; Bruce, M. I.; Matheson, T. W. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 4, Chapter 32.3, pp 775–795. (b) Albers, M. O.; Robinson, D. J.; Singleton, E. *Coord. Chem. Rev.* **1987**, *79*, 1.

(5) (a) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A.* **1971**, 2376. (b) Ashby, G. S.; Bruce, M. I.; Tomkins, I. B.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1003. (c) Bruce, M. I.; Cifuentes, M. P.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1989**, *359*, 379. (d) Treichel, P. M.; Komar, D. A. *Synth. React. Inorg. Met.-Org. Chem.* **1980**, *10*, 205. (e) Bruce, M. I.; Humphrey, M. G.; Swincer, A. G.; Wallis, R. C. *Aust. J. Chem.* **1984**, *37*, 1747. (f) Davies, S. G.; Scott, F. *J. Organomet. Chem.* **1980**, *188*, C41. (g) Joslin, F. L.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 521. (f) Haines, R. J.; du Preez, A. L. *J. Organomet. Chem.* **1975**, *84*, 357.

(6) Some related ruthenium systems: (a) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274. (b) Bleeke, J. R.; Rauscher, D. J. *Organometallics* **1988**, *7*, 2328. (c) Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308.

(7) Ernst, M. F.; Roddick, D. M. *Organometallics* **1990**, *9*, 1586.

(8) Merwin, R. K.; Roddick, D. M., unpublished results.

0276-7333/92/2311-3417$03.00/0