Bridged Ferrocenes. 11.[1] 2,2′- and 3,3′-Trimethylene[1.1]ferrocenophane

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The preparation and structural determination of the title compounds are described. The significant features of the structures are the directions of the ring tilts, which play a role in the interactions between the ferrocene units. The redox potentials of these and similar compounds are given and are interpreted according to the structures. The NMR spectra indicate that the [1.1] methylene protons of the 3,3′-bridged derivative interconvert rapidly as they do in the nonbridged parent. The 2,2′-bridged derivative has rigid [1.1] methylenes.

Introduction

A significant number of investigations of the preparation and properties of bridged ferrocenes have been reported.[2] Trimethylene bridges have been of particular interest since they are too short to span the distance between the cyclopentadienyl rings, thereby forcing the rings to tilt with respect to each other and to come closer to the iron atom. The effects of these bridges on such properties as Mössbauer spectra[3] and redox potentials[2] have been correlated with the iron-to-ring distances. The tilting is also accompanied by a rehybridization of iron orbitals so that three coplanar orbitals are projected toward the opening of the tilted rings.[4,5] This implies an increased reactivity of the iron toward such reactions as protonation[6,7] and complexation with Lewis acids.[8]

Dinuclear ferrocenes such as [0.0]ferrocenophane, I (all of the structures are illustrated in the four figures), and [1.1]ferrocenophane, II, have found interest in investigations of the interaction of the iron atoms[9] and in investigations of the reaction with very strong acids to form the dications and dihydrogen,[10,11] presumably via an intermediate containing a proton on each iron atom. A direct iron–iron interaction has been established[9] in the monocation of I. This occurs apparently because of the removal of an electron from an antibonding orbital.[12]

The inclusion of trimethylene bridges at appropriate positions should either enhance or decrease the interaction of the iron atoms depending on the directions of the projected iron orbitals. Repulsion of the iron atoms, which is too small to be conclusively observed in the neutral, nonbridged species, may also be enhanced or decreased with appropriate bridge substitution. Similar arguments can be advanced for increasing or decreasing the rate of hydrogen formation from appropriately bridged ferrocenophanes. Since protonation is accompanied[13,14] by ring tilting, pretilting may enhance the ease of protonation. Furthermore, the orientation of the protons on the irons is probably determined by the directions of the tilt openings imposed by the trimethylene bridges. Thus, the rate of dehydrogenation of the diprotonated species can be controlled by appropriate bridges.[11]

It is for these reasons that we began to investigate the bridged ferrocenophanes. We report at this time the preparation and some of the properties of 2,2′-trimethylene[1.1]ferrocenophane, III, and of 3,3′-trimethylene[1.1]ferrocenophane, IV.

Results

Compounds III and IV were prepared by modifications of the procedure for the preparation of II by Mueller-Westerhoff and co-workers.[15] Starting with 1,1′-trimethyleneferrocene, VI, a mixture of the dilithio derivatives was prepared by using *n*-butyllithium and *N*,*N*,-*N*′,*N*′-tetramethylethylenediamine (TMEDA). This mixture had been shown[16] to consist predominantly of the 2,2′- and the 3,3′-dilithio derivatives. If potassium *tert*-butoxide was substituted for the TMEDA, the 3,3′-dilithio derivative

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Table I. Fractional Coordinates for III[a]

atom	*x/a*	*y/b*	*z/c*	*B*, pm²	atom	*x/a*	*y/b*	*z/c*	*B*, pm²
Fe1	5390 (2)	1445 (2)	10312	292 (9)	C14	436 (2)	66 (2)	815 (4)	51 (7)
Fe2	5376 (2)	3711 (2)	8937 (7)	371 (9)	C15	404 (2)	114 (2)	950 (4)	59 (8)
Fe1A	8108 (2)	1158 (2)	3880 (7)	347 (9)	C1A	833 (1)	173 (1)	585 (4)	47 (6)
Fe2A	7645 (2)	3422 (2)	3721 (7)	334 (9)	C2A	813 (1)	108 (1)	635 (3)	30 (5)
C1	569 (1)	177 (1)	810 (3)	35 (5)	C3A	860 (1)	64 (1)	562 (4)	49 (6)
C2	541 (1)	114 (1)	800 (3)	25 (4)	C4A	897 (1)	99 (1)	461 (4)	43 (6)
C3	572 (1)	68 (1)	908 (3)	28 (4)	C5A	886 (1)	166 (1)	475 (4)	47 (6)
C4	620 (1)	104 (1)	973 (3)	43 (6)	C1A′	732 (1)	148 (1)	283 (3)	26 (4)
C5	620 (1)	170 (1)	913 (3)	32 (5)	C2A′	726 (1)	89 (1)	355 (4)	41 (4)
C1′	466 (1)	203 (1)	1100 (3)	27 (4)	C3A′	760 (2)	43 (2)	288 (4)	49 (6)
C2′	448 (1)	140 (1)	1072 (3)	33 (5)	C4A′	796 (2)	74 (2)	166 (5)	58 (8)
C3′	481 (1)	99 (1)	1185 (4)	44 (6)	C5A′	778 (1)	144 (1)	172 (4)	43 (6)
C4′	522 (1)	136 (1)	1280 (4)	40 (6)	C6A	812 (1)	300 (1)	559 (3)	32 (5)
C5′	509 (1)	202 (1)	1235 (4)	46 (6)	C7A	777 (1)	356 (1)	620 (4)	41 (6)
C6	573 (1)	302 (1)	745 (3)	32 (5)	C8A	801 (1)	413 (1)	532 (5)	47 (6)
C7	548 (2)	356 (2)	651 (5)	58 (8)	C9A	847 (1)	390 (1)	418 (4)	44 (6)
C8	582 (1)	411 (1)	706 (4)	43 (6)	C10A	855 (1)	319 (1)	438 (3)	39 (6)
C9	624 (1)	391 (1)	829 (4)	44 (6)	C6A′	705 (1)	278 (1)	278 (3)	28 (4)
C10	618 (1)	325 (1)	845 (3)	28 (4)	C7A′	675 (1)	330 (1)	341 (4)	47 (6)
C6′	468 (1)	334 (1)	1036 (4)	42 (5)	C8A′	693 (2)	389 (2)	266 (4)	51 (6)
C7′	447 (2)	384 (2)	925 (5)	60 (8)	C9A′	738 (1)	369 (2)	146 (4)	49 (6)
C8′	478 (1)	442 (1)	972 (4)	50 (6)	C10A′	746 (1)	298 (1)	159 (3)	34 (5)
C9′	517 (2)	427 (2)	1100 (4)	51 (5)	C11A	803 (1)	235 (1)	653 (4)	42 (6)
C10′	511 (2)	356 (1)	1133 (4)	44 (6)	C12A	691 (1)	207 (1)	333 (3)	39 (6)
C11	552 (1)	233 (1)	701 (3)	35 (5)	C13A	764 (2)	90 (2)	732 (4)	51 (6)
C12	440 (1)	265 (1)	1026 (4)	37 (5)	C14A	713 (2)	45 (2)	647 (4)	56 (7)
C13	480 (2)	97 (2)	706 (5)	53 (7)	C15A	680 (1)	70 (2)	496 (4)	47 (6)

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
H3	562	21	930	H3A	864	17	586
H4	651	87	1052	H4A	928	79	384
H5	650	205	941	H5A	911	202	423
H3′	475	51	1197	H3A′	760	−5	318
H4′	553	119	1360	H4A′	827	53	91
H5′	528	242	1287	H5A′	797	180	106
H7	515	354	566	H7A	744	355	704
H8	578	457	665	H8A	788	460	548
H9	652	420	893	H9A	870	418	338
H10	644	297	920	H10A	885	290	379
H7′	416	378	834	H7A′	644	328	432
H8′	472	486	921	H8A′	678	434	290
H9′	544	459	1159	H9A′	761	398	68
H10′	536	330	1214	H10A′	775	270	94
H11A	568	223	589	H11AA	758	227	661
H11B	506	234	698	H11AB	820	242	766
H12A	435	256	906	H12AA	690	208	456
H12B	398	270	1078	H12AB	649	197	290
H13A	490	66	615	H13AA	781	66	829
H13B	461	137	659	H13AB	744	131	770
H14A	402	47	746	H14AA	681	37	732
H14B	457	31	877	H14AB	734	3	616
H15A	371	89	1009	H15AA	652	35	455
H15B	385	152	890	H15AB	655	110	527

[a] The coordinates of the iron atoms are multiplied by 10^4. The coordinates of the other atoms are multiplied by 10^3. Errors are not given for the hydrogen coordinates since they were not refined. The isotropic thermal factors are B_{eqv} for the iron atoms and are divided by 10^2 and B_{iso} for the carbon atoms and are divided by 10^3.

was essentially the only one formed. Reaction of the mixture of lithio derivatives with 6-(dimethylamino)fulvene gave a separable mixture of VII and VIII and small quantities of the monosubstituted fulvenyl derivatives. The structures of VII and VIII were ascertained by their NMR spectra and by their subsequent reactions. Reaction of VII and VIII with lithium tri-*sec*-butylborohydride gave the dianions, which reacted further with the ferrous chloride–tetrahydrofuran complex ($FeCl_2$·THF) to give III and IV. The structures of the final products were ascertained by X-ray crystallography.

The fractional atomic coordinates for III and IV are given in Tables I and II. The thermal parameters and the observed and calculated structure factors are available as supplementary material. ORTEP diagrams of the non-hydrogen atoms of III and IV are given in Figures 1 and 2. Selected bond distances and angles are given in Tables III–VI. The least-squares planes of the rings and the dihedral angles between the planes are presented in Table VII. The redox potentials of III, IV, and several other compounds are given in Table VIII.

Because of the difficulty in obtaining good single crystals of III, a rather small number of reflections with $F > 3\sigma(F)$ could be observed, and the atomic parameters derived have large standard deviations. Thus, the errors for III are large, and only gross features of the molecule can be deduced with confidence: e.g., the molecular structure and the general orientation of the rings, in particular the directions of the ring-tilt openings.

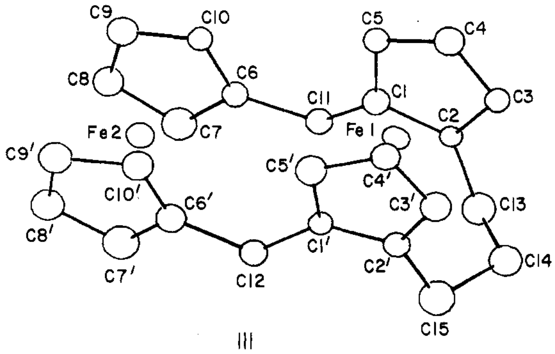
Discussion

Views of the molecular structures of III and IV are

Table II. Fractional Coordinates for IV

atom	x/a	y/b	z/c	B, pm^2
Fe1	18422 (3)	52319 (7)	64990 (5)	248 (1)
Fe2	39072 (3)	51822 (7)	61278 (5)	217 (1)
C1	2442 (2)	6395 (6)	7848 (4)	30 (1)
C2	1951 (2)	5647 (7)	8369 (4)	35 (1)
C3	1415 (2)	6420 (7)	7779 (5)	41 (2)
C4	1568 (3)	7696 (7)	6932 (7)	46 (2)
C5	2198 (3)	7692 (6)	6954 (6)	40 (1)
C1′	2220 (2)	3117 (5)	5683 (4)	25 (1)
C2′	1735 (2)	2576 (6)	6350 (5)	31 (1)
C3′	1213 (2)	3481 (7)	5862 (5)	35 (1)
C4′	1358 (3)	4560 (8)	4858 (5)	39 (1)
C5′	1971 (2)	4363 (7)	4754 (4)	33 (1)
C6	3585 (2)	6352 (5)	7621 (3)	23 (1)
C7	4162 (2)	5639 (7)	7987 (4)	30 (1)
C8	4570 (2)	6442 (7)	7249 (5)	35 (1)
C9	4244 (2)	7660 (6)	6453 (5)	33 (1)
C10	3642 (2)	7620 (5)	6676 (4)	28 (1)
C6′	3358 (2)	3127 (5)	5471 (4)	25 (1)
C7′	3941 (2)	2510 (6)	5865 (4)	29 (1)
C8′	4343 (3)	3388 (7)	5186 (5)	34 (1)
C9′	4016 (2)	4543 (6)	4326 (4)	31 (1)
C10′	3405 (2)	4405 (6)	4502 (4)	27 (1)
C11	3071 (2)	5922 (6)	8332 (4)	28 (1)
C12	2826 (2)	2317 (6)	5950 (4)	26 (1)
C13	783 (3)	5876 (10)	8007 (7)	60 (3)
C14A	413 (6)	5084 (16)	6868 (11)	44 (2)
C14B	629 (6)	4074 (17)	7708 (11)	48 (2)
C15	615 (3)	3375 (8)	6348 (6)	48 (2)
H2	200 (2)	475 (5)	896 (4)	2 (1)
H4	138 (2)	837 (7)	636 (4)	3 (1)
H5	241 (3)	834 (8)	637 (5)	6 (1)
H2′	176 (2)	169 (6)	702 (5)	3 (1)
H4′	113 (3)	520 (7)	443 (5)	4 (1)
H5′	215 (3)	498 (7)	416 (5)	4 (1)
H7	426 (2)	477 (5)	854 (4)	1 (1)
H8	501 (3)	637 (8)	735 (5)	5 (1)
H9	445 (2)	837 (6)	583 (4)	3 (1)
H10	330 (2)	813 (4)	622 (3)	0 (1)
H7′	403 (2)	176 (6)	645 (4)	2 (1)
H8′	467 (2)	326 (7)	527 (5)	4 (1)
H9′	416 (3)	537 (7)	371 (5)	5 (1)
H10′	307 (2)	506 (5)	406 (4)	1 (1)
H11A	313 (2)	475 (5)	849 (3)	1 (1)
H11B	318 (2)	650 (7)	919 (5)	4 (1)
H12A	279 (2)	114 (6)	562 (4)	2 (1)
H12B	292 (2)	217 (5)	678 (4)	1 (1)

[a] The coordinates of the iron atoms are multiplied by 10^5. The coordinates of the carbon atoms are multiplied by 10^4. The coordinates of the hydrogen atoms are multiplied by 10^3. The thermal factors are B_{eqv} for the iron atoms and for the carbons except C14A and C14B and are divided by 10^2 for the iron atoms and 10^3 for the carbon atoms. The thermal factors are B_{iso} for C14A and C14B and the hydrogen atoms and are divided by 10^4.



III

Figure 1. ORTEP diagram of non-hydrogen atoms of compound III. The ellipsoids and spheres represent 25% probabilities.

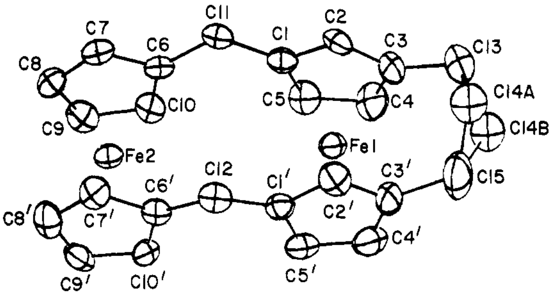


Figure 2. ORTEP diagram of non-hydrogen atoms of compound IV. The ellipsoids represent 50% probabilities.

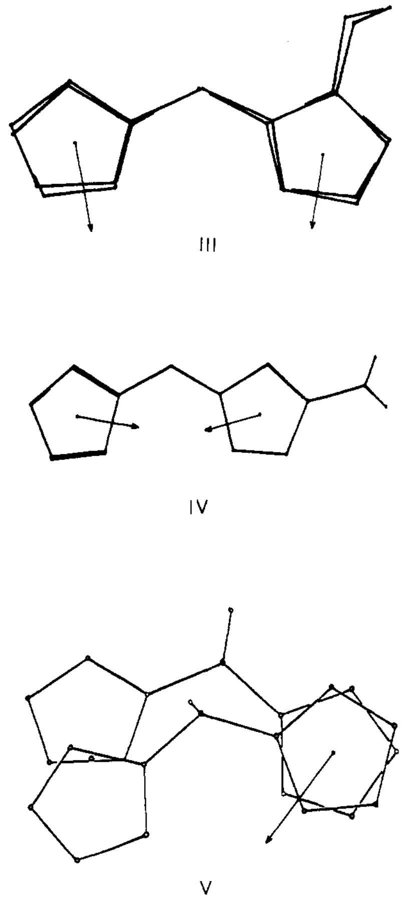


Figure 3. ORTEP diagrams of non-hydrogen atoms of compounds III, IV, and V show relative twisting of the two ferrocene units and the directions (arrows) of the ring-tilt openings.

compared to a similar view of the 11,12-dimethyl derivative of the nonbridged compound V[17] in Figure 3. The ferrocene units in V are twisted about 31° with respect to each other. This twist reduces the close approach of the 5,5′-hydrogens to the 10,10′-hydrogens and of the endo hydrogens on C11 and C12. In the absence of twisting the pairs of hydrogen atoms would be about 100 pm apart. As a result of the twisting, the 5- and 10-hydrogens are separated by 251 pm, the 5- and 10′-hydrogens are separated by 222 pm, and the endo hydrogens on C11 and C12 are separated by 223 pm. The twisting is accompanied by a staggering of the cyclopentadienyl rings in each unit by 23°. In III and IV, the trimethylene bridges inhibit the staggering of the rings, and, consequently the same kind of twisting does not occur. Separation of the 5- and 10-hydrogens (191 pm in III and 208 pm, in IV) and of the endo hydrogens (230 pm in III and 268 pm in IV) is accomplished by several means. The tilting of the pairs of cyclopentadienyl rings are different, the bridged pairs

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Table III. Selected Bond Distances for III (pm)

molecule I		molecule II	
Fe1-Fe2	476.6 (6)	Fe1A-Fe2A	473.8 (6)
C1-C11	149 (4)	C1A-C11A	153 (4)
C1′-C12	152 (3)	C1A′-C12A	156 (3)
C6-C11	152 (3)	C6A-C11A	153 (4)
C6′-C12	155 (3)	C6A′-C12A	154 (3)
Fe1-C1	203 (3)	Fe1A-C1A	204 (3)
Fe1-C2	198 (2)	Fe1A-C2A	202 (3)
Fe1-C3	199 (2)	Fe1A-C3A	207 (3)
Fe1-C4	200 (3)	Fe1A-C4A	200 (3)
Fe1-C5	207 (2)	Fe1A-C5A	206 (3)
Fe1-C1′	207 (2)	Fe1A-C1A′	202 (3)
Fe1-C2′	201 (3)	Fe1A-C2A′	194 (3)
Fe1-C3′	200 (3)	Fe1A-C3A′	202 (3)
Fe1-C4′	206 (3)	Fe1A-C4A′	203 (4)
Fe1-C5′	213 (3)	Fe1A-C5A′	197 (3)
C1-C2	142 (3)	C1A-C2A	145 (4)
C2-C3	146 (3)	C2A-C3A	148 (4)
C3-C4	138 (3)	C3A-C4A	135 (4)
C4-C5	143 (4)	C4A-C5A	139 (4)
C5-C1	139 (4)	C5A-C1A	148 (4)
C1′-C2′	136 (3)	C1A′-C2A′	135 (3)
C2′-C3′	142 (4)	C2A′-C3A′	132 (4)
C3′-C4′	139 (4)	C3A′-C4A′	142 (4)
C4′-C5′	143 (4)	C4A′-C5A′	148 (5)
C5′-C1′	145 (4)	C5A′-C1A′	135 (4)
C2-C13	158 (4)	C2A-C13A	138 (4)
C13-C14	145 (5)	C13A-C14A	160 (5)
C14-C15	162 (4)	C14A-C15A	151 (4)
C15-C2′	148 (4)	C15A-C2A′	158 (4)
Fe2-C6	202 (3)	Fe2A-C6A	203 (3)
Fe2-C7	201 (4)	Fe2A-C7A	206 (3)
Fe2-C8	199 (3)	Fe2A-C8A	210 (3)
Fe2-C9	200 (3)	Fe2A-C9A	208 (3)
Fe2-C10	203 (2)	Fe2A-C10A	210 (3)
Fe2-C6′	204 (3)	Fe2A-C6A′	200 (2)
Fe2-C7′	201 (4)	Fe2A-C7A′	197 (3)
Fe2-C8′	205 (3)	Fe2A-C8A′	202 (3)
Fe2-C9′	208 (3)	Fe2A-C9A′	200 (3)
Fe2-C10′	205 (3)	Fe2A-C10A′	200 (3)
C6-C7	145 (4)	C6A-C7A	147 (4)
C7-C8	144 (4)	C7A-C8A	146 (4)
C8-C9	141 (4)	C8A-C9A	145 (4)
C9-C10	137 (4)	C9A-C10A	148 (4)
C10-C6	136 (3)	C10A-C6A	141 (4)
C6′-C7′	143 (5)	C6A′-C7A′	136 (4)
C7′-C8′	142 (4)	C7A′-C8A′	140 (4)
C8′-C9′	137 (4)	C8A′-C9A′	144 (4)
C9′-C10′	149 (4)	C9A′-C10A′	147 (4)
C10′-C6′	130 (4)	C10A′-C6A′	138 (3)

Table IV. Selected Bond Distances for IV (pm)

Fe1-Fe2	474.9 (1)		
C1-C11	149.8 (6)	C11-C6	150.9 (6)
C1′-C12	149.4 (6)	C12-C6′	150.1 (6)
C11-H11A	91 (4)	C12-H12A	96 (4)
C11-H11B	103 (5)	C12-H12B	90 (4)
Fe1-C1	205.6 (4)	Fe2-C6	205.2 (4)
Fe1-C2	202.6 (5)	Fe2-C7	204.5 (4)
Fe1-C3	199.8 (6)	Fe2-C8	203.9 (5)
Fe1-C4	203.0 (6)	Fe2-C9	202.9 (4)
Fe1-C5	205.4 (5)	Fe2-C10	204.2 (4)
Fe1-C1′	205.8 (4)	Fe2-C6′	205.5 (4)
Fe1-C2′	201.8 (4)	Fe2-C7′	203.5 (4)
Fe1-C3′	199.9 (5)	Fe2-C8′	202.2 (6)
Fe1-C4′	202.6 (5)	Fe2-C9′	204.9 (4)
Fe1-C5′	205.0 (5)	Fe2-C10′	205.2 (4)
C1-C2	142.5 (7)	C6-C7	142.3 (6)
C2-C3	142.3 (8)	C7-C8	143.1 (7)
C3-C4	140.1 (8)	C8-C9	140.2 (7)
C4-C5	142.5 (8)	C9-C10	141.5 (6)
C5-C1	143.3 (7)	C10-C6	141.6 (5)
C1′-C2′	144.6 (6)	C6′-C7′	141.4 (6)
C2′-C3′	140.9 (7)	C7′-C8′	140.5 (7)
C3′-C4′	142.6 (7)	C8′-C9′	141.2 (7)
C4′-C5′	141.5 (8)	C9′-C10′	142.5 (7)
C5′-C1′	143.5 (6)	C10′-C6′	143.5 (5)
C3-C13	153.9 (8)		
C13-C14A	152 (1)		
C13-C14B	143 (1)		
C14A-C15	150 (1)		
C14B-C15	156 (1)		
C15-C8	151.7 (7)		
C2-H2	93 (4)	C7-H7	89 (4)
		C8-H8	98 (6)
C4-H4	86 (5)	C9-H9	102 (4)
C5-H5	97 (6)	C10-H10	94 (3)
C2′-H2′	98 (5)	C7′-H7′	85 (4)
		C8′-H8′	75 (5)
C4′-H4′	80 (5)	C9′-H9′	100 (5)
C5′-H5′	93 (5)	C10′-H10′	98 (4)

being 12° and 10°, respectively, and the others 4° and 3°, respectively. A ring tilt of 3° is also found for V. (The arrows in Figure 3 give the directions of the tilts, with the arrowheads pointing towards the openings.) Consequently the relevant C–H vectors are not coplanar. Further separation is accomplished by the opening of the C1–C11–C6 and the corresponding C1′–C12–C6′ angles. In V, these angles are larger than normal, 117°, but in III and IV the angles are still larger, 122°.

The NMR spectra of II and of IV have single sharp peaks for the protons of the [1.1] methylene groups, indicating that both molecules are sufficiently flexible to equilibrate the endo and exo protons in the NMR time scale. The spectrum of III, on the other hand, is that of a more rigid molecule. The peak for the protons of the [1.1] methylenes is split into an AB quartet. Dreiding models indicate a large difference in flexibility between II and III and a small difference between III and IV. Since IV interconverts like II, but not necessarily as fast, and III does not interconvert, the flexibility illustrated by the models cannot be a significant test. Recently it was shown[18] that the 2-ethyl derivative of II has noninterconverting [1.1] methylenes, while the 3-ethyl derivative shows rapid interconversion. In these compounds the flexibilities of the models are the same as for II. It was noted[18] that substituents in the 2-position sterically interfere with the interconversion. The same would be true of the 2,2′ bridge.

The redox potentials, which are listed in Table VIII, are interpretable as a consequence of the interaction between the two parts of the molecules, depending upon their geometries. The potential for ferrocene itself is used as a reference point for the discussion. In I, the interaction between the two ferrocene units is strongest as is demonstrated by the reduction of the first potential to 130 mV by the electron-donating influence of the second ferrocene unit and the increase of the second potential to 720 mV by the electron-withdrawing influence of the ferrocenium unit.[19] The first potential of II is lowered and the second is increased compared to ferrocene, but not as much as in I, since the relative influences of the ferrocene and the ferrocenium units are decreased both by the lack of conjugation and by the increased distance between the two units. In III and IV, the first potentials are lower than in II by virtue of the trimethylene bridges.[2] The potential of trimethyleneferrocene, VI, is lower than that of ferrocene by 73 mV. Addition of the trimethylene bridge to II, forming III and IV, also lowers the first potential. The effect of the addition of the trimethylene bridge to II, however, is not strictly comparable to the addition of a

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Table V. Selected Bond Angles for III (deg)

molecule I		molecule II	
C1–C11–C6	120 (2)	C1A–C11A–C6A	118 (3)
C1′–C12–C6′	127 (2)	C1A′–C12A–C6A′	122 (2)
C1–C2–C3	111 (2)	C1A–C2A–C3A	104 (2)
C2–C3–C4	103 (2)	C2A–C3A–C4A	110 (3)
C3–C4–C5	112 (3)	C3A–C4A–C5A	111 (3)
C4–C5–C1	108 (2)	C4A–C5A–C1A	107 (3)
C5–C1–C2	106 (2)	C5A–C1A–C2A	107 (2)
C1′–C2′–C3′	107 (2)	C1A′–C2A′–C3A′	114 (3)
C2′–C3′–C4′	112 (3)	C2A′–C3A′–C4A′	106 (3)
C3′–C4′–C5′	104 (3)	C3A′–C4A′–C5A′	105 (3)
C4′–C5′–C1′	109 (3)	C4A′–C5A′–C1A′	107 (3)
C5′–C1′–C2′	107 (2)	C5A′–C1A′–C2A′	107 (2)
C2–C1–C11	123 (2)	C2A–C1A–C11A	122 (3)
C5–C1–C11	129 (2)	C5A–C1A–C11A	130 (3)
C7–C6–C11	118 (3)	C7A–C6A–C11A	116 (2)
C10–C6–C11	133 (2)	C10A–C6A–C11A	132 (2)
C2′–C1′–C12	129 (2)	C2A′–C1A′–C12A	121 (2)
C5′–C1′–C12	123 (2)	C5A′–C1A′–C12A	132 (2)
C7′–C6′–C12	119 (3)	C7A′–C6A′–C12A	123 (2)
C10′–C6′–C12	129 (3)	C10A′–C6A′–C12A	128 (1)
C1–C2–C13	127 (2)	C1A–C2A–C13A	129 (3)
C3–C2–C13	122 (2)	C3A–C2A–C13A	127 (3)
C2–C13–C14	111 (3)	C2A–C13A–C14A	116 (3)
C13–C14–C15	116 (3)	C13A–C14A–C15A	119 (3)
C14–C15–C2′	113 (3)	C14A–C15A–C2A′	112 (3)
C1′–C2′–C15	129 (3)	C1A′–C2A′–C15A	127 (2)
C3′–C2′–C15	124 (3)	C3A′–C2A′–C15A	119 (3)
C6–C7–C8	104 (3)	C6A–C7A–C8A	106 (3)
C7–C8–C9	109 (3)	C7A–C8A–C9A	108 (3)
C8–C9–C10	107 (3)	C8A–C9A–C10A	109 (3)
C9–C10–C6	111 (2)	C9A–C10A–C6A	106 (2)
C10–C6–C7	109 (2)	C10A–C6A–C7A	111 (2)
C6′–C7′–C8′	106 (3)	C6A′–C7A′–C8A′	112 (3)
C7′–C8′–C9′	108 (3)	C7A′–C8A′–C9A′	104 (3)
C8′–C9′–C10′	107 (3)	C8A′–C9A′–C10A′	108 (3)
C9′–C10′–C6′	107 (3)	C9A′–C10A′–C6A′	106 (2)
C10′–C6′–C7′	112 (3)	C10A′–C6A′–C7A′	109 (2)

Table VI. Selected Bond Angles for IV (deg)

C1–C11–C6	122.2 (4)	C1′–C12–C6′	121.9 (4)
C1–C11–H11A	114 (3)	C1′–C12–H12A	106 (3)
C1–C11–H11B	108 (3)	C1′–C12–H12B	109 (3)
C6–C11–H11A	102 (2)	C6′–C12–H12A	106 (2)
C6–C11–H11B	105 (3)	C6′–C12–H12B	108 (3)
H11A–C11–H11B	104 (4)	H12A–C12–H12B	105 (3)
C1–C2–C3	109.1 (5)	C6–C7–C8	108.9 (4)
C2–C3–C4	107.7 (5)	C7–C8–C9	106.8 (5)
C3–C4–C5	108.6 (5)	C8–C9–C10	109.1 (4)
C4–C5–C1	108.2 (5)	C9–C10–C6	108.5 (4)
C5–C1–C2	106.3 (5)	C10–C6–C7	106.7 (4)
C1′–C2′–C3′	109.4 (4)	C6′–C7′–C8′	109.4 (4)
C2′–C3′–C4′	107.2 (4)	C7′–C8′–C9′	108.2 (5)
C3′–C4′–C5′	108.9 (5)	C8′–C9′–C10′	107.7 (4)
C4′–C5′–C1′	108.6 (4)	C9′–C10′–C6′	108.1 (4)
C5′–C1′–C2′	106.0 (4)	C10′–C6′–C7′	106.6 (4)
C1–C2–H2	122 (3)	C6–C7–H7	126 (3)
C3–C2–H2	129 (3)	C8–C7–H7	125 (3)
C2–C3–C13	125.4 (6)	C7–C8–H8	129 (3)
C4–C3–C13	126.9 (6)	C9–C8–H8	124 (3)
C3–C4–H4	137 (4)	C8–C9–H9	120 (3)
C5–C4–H4	114 (3)	C10–C9–H9	131 (3)
C4–C5–H5	124 (4)	C9–C10–H10	130 (2)
C1–C5–H5	127 (4)	C6–C10–H10	121 (2)
C5–C1–C11	131.7 (4)	C10–C6–C11	131.3 (4)
C2–C1–C11	121.7 (4)	C7–C6–C11	106.7 (4)
C1′–C2′–H2′	126 (3)	C6′–C7′–H7′	125 (3)
C3′–C2′–H2′	125 (3)	C8′–C7′–H7′	126 (3)
C2′–C3′–C15	126.2 (5)	C7′–C8′–H8′	125 (4)
C4′–C3′–C15	126.6 (5)	C9′–C8′–H8′	126 (4)
C3′–C4′–H4′	126 (4)	C8′–C9′–H9′	130 (3)
C5′–C4′–H4′	125 (4)	C10′–C9′–H9′	122 (3)
C4′–C5′–H5′	122 (4)	C9′–C10′–H10′	128 (2)
C1′–C5′–H5′	130 (4)	C6′–C10′–H10′	124 (2)
C2′–C1′–C12	121.9 (4)	C7′–C6′–C12	121.6 (4)
C5′–C1′–C12	131.9 (4)	C10′–C6′–C12	131.4 (4)

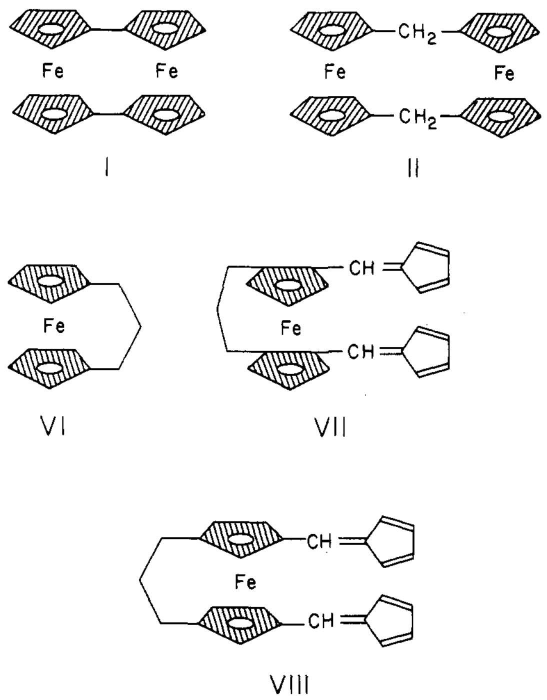

Figure 4. Representations of bridged ferrocenes.

trimethylene bridge to ferrocene because introduction of the bridge to II is also accompanied by a change in the interaction of the two ferrocene units of the molecule because of the relative twisting of the two units in II and lack of such twisting in III and IV.

Of greater significance is the observation that the first potential of IV is lower than the first potential of III by 67 mV. Since the overall geometries of the two bridged compounds are dominated by the presence of the trimethylene bridges, they are expected to behave similarly, and the difference in potentials is necessarily due to a special condition, such as the direction of the tilt openings. In IV, as evident from the crystal structures, they are directed toward each other to a considerably greater extent than in III. Evidently, this causes the interaction between the two ferrocene units to be greater in IV than in III, and the first potential is lower. However, the second potentials are not similarly influenced. They are essentially the same for II, III, and IV. This implies that once the first electron is removed, that is, when one of the units is a ferrocenium (the bridged units in III and IV), there is no difference in effect due to the presence of bridges, tilting, or the direction of projected orbitals. This is consistent with the Mössbauer spectra which show that the electron distribution around the iron atom of ferrocene is not spherical, while in ferrocenium ions the electron distribution is essentially spherical.[20] Similar Mössbauer results have been obtained for bridged ferrocenes[3] and bridged ferroceniums.[3,21] This phenomenon deserves further investigation.

Experimental Section

Reactions and distillations were carried out under nitrogen. All solvents and liquid reactants were distilled before use: THF from $LiAlH_4$ directly before use, hexanes, benzene, dimethylformamide (DMF), and TMEDA from CaH_2, and dimethyl sulfate (DMS) without a drying agent. Acetonitrile (Spectrophotometric Grade, Aldrich Gold Label) was triply distilled directly before

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Table VII. Least-Squares Planes

Equations for Distances from Planes (pm)

Compound III	
ring I: C1-C5	$D = 1270.55x - 542.52y - 623.48z - 124.81$
ring II: C1′-C5′	$D = 1587.80x - 184.73y - 550.70z - 95.09$
ring III: C6-C10	$D = 1488.13x - 308.27y - 580.03z - 329.03$
ring IV: C6′-C10′	$D = 1558.86x - 433.42y - 540.08z - 28.39$
ring V: C1A-C5A	$D = -1331.82x - 167.88y - 639.16z + 1510.19$
ring VI: C1A′-C5A′	$D = -1520.09x - 418.04y - 557.15z + 1335.39$
ring VII: C6A-C10A	$D = -1503.42x - 298.76y - 575.29z + 1631.84$
ring VIII: C6A′-C10A′	$D = -1559.51x - 230.04y - 559.22z + 1319.30$
Compound IV	
ring I: C1-C5	$D = 31.75x - 528.20y - 764.84z + 930.91$
ring II: C1′-C5′	$D = -315.29x - 564.77y - 673.03z + 628.28$
ring III: C6-C10	$D = -225.33x - 538.54y - 726.97z + 977.35$
ring IV: C6′-C10′	$D = -73.41x - 548.57y - 728.11z + 594.28$

Distances of Irons from Planes (pm)

ring I		ring II		ring III		ring IV	
Compound III							
Fe1	161.3 (2)	Fe1	166.2 (2)	Fe2	161.7 (1)	Fe2	166.2 (5)
Fe1A	162.9 (5)	Fe1A	161.7 (5)	Fe2A	166.3 (5)	Fe2A	159.7 (5)
Compound IV							
Fe1	163.3 (1)	Fe1	162.7 (1)	Fe2	164.8 (1)	Fe2	164.9 (1)

Angles between Planes (deg)

Compound III			
ring I-ring II	14.1	ring V-ring VI	10.4
ring I-ring III	9.2	ring V-ring VII	7.4
ring I-ring IV	10.1	ring V-ring VIII	8.4
ring II-ring III	4.8	ring VI-ring VII	3.6
ring II-ring IV	7.1	ring VI-ring VIII	5.4
ring III-ring IV	4.9	ring VII-ring VIII	2.3
Compound IV			
ring I-ring II	10.0	ring II-ring III	4.0
ring I-ring III	6.7	ring II-ring IV	6.6
ring I-ring IV	3.5	ring III-ring IV	3.9

Table VIII. Redox Potentials vs. SCE (mV)

	potentials	
compd	first	second
ferrocene[17]	400	
I[17]	130	720
II	298	498
III	255	488
IV	188	495
VI[3]	327	

use, first from CaH_2, then from P_2O_5, and finally from CaH_2. Tetrabutylammonium perchlorate was used without purification. Column chromatography was carried out with Fisher "Adsorption Alumina". Compound VI was available in our laboratory as a result of previous work.[2]

Cyclic voltammetry was performed with an IBM EC 225 voltammetric analyzer equipped with a YEW Model 3022 A4 X-Y recorder. Solutions were 0.1 M in electrolyte. Samples were dissolved in benzene and aliquots (0.01–0.03 mL) were added via syringe to electrolytic cells containing 0.5 mL of 0.1 M $N(C_4H_9)_4ClO_4$ in CH_3CN so that the substrate concentration was approximately 5×10^{-4} M. The cells were equipped with platinum bead electrodes and a SCE in a fritted compartment containing electrolyte solution. Electrochemical reversibility of the observed oxidations was assessed qualitatively by the anodic–cathodic peak separations and the relative current densities. We are indebted to the late Dr. Ichiro Fujita for his advice on obtaining the redox potentials.

NMR spectra were recorded on a Varian CFT-20 instrument (80 MHz). The NMR peak assignments, given only when reasonably certain, are based on the shifts expected from the ring tilts as determined in the crystal structures.

Crystals of III and IV were mounted along their long axes for the collection of the diffraction intensity data on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 71.07 pm). The crystal data are given in Table IX. Intensities were collected by using θ–2θ scans and were corrected for Lorentz, polarization and absorption effects.

From the systematic absences, the space group of III was found to be either $Pna2_1$ or $Pnma$. $Pna2_1$ was determined as correct from the success of the refinement using that space group and from the inability to obtain a refinement using $Pnma$. The observed systematic absences uniquely determine the space group of IV as $P2_1/c$.

The iron atoms of III were located by using MULTAN-80,[22] and the iron atoms of IV were located from Patterson maps using the SHELX-76 crystallographic computing package.[23] The remaining atomic positions for both compounds were obtained from successive difference Fourier maps using SHELX-76. The atomic scattering factors for iron including components for anomalous dispersion were taken from tabulations of Doyle and Turner[24] and Cromer and Liberman.[25] Those for hydrogen are from Stewart et al.[26] The other atomic scattering factors are from Cromer and Mann.[27]

Anisotropic thermal factors were determined only for the iron atoms of III since the limited number of reflections with significant intensities and the large number of parameters precluded getting meaningful results for anisotropic thermal factors for the other

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Table IX. Crystal Data

	III	IV
mol formula	$C_{25}H_{24}Fe_2$	$C_{25}H_{24}Fe_2$
mol wt	438.24	438.24
space group	$Pna2_1$	$P2_1/c$
a, pm	2175.4 (9)	2266.7 (5)
b, pm	2044.6 (8)	752.8 (2)
c, pm	812.8 (4)	1079.7 (2)
α, deg	90.00	90.00
β, deg	90.00	97.34 (2)
γ, deg	90.00	90.00
V, nm^3	3.6149	1.8274
Z	8	4
cryst size, mm × mm × mm	0.27 × 0.27 × 0.2	0.42 × 0.3 × 0.06
ρ_{calcd}, g/cm^3	1.611	1.593
abs coeff, cm^{-1}	15.83	15.65
2θ range, deg	2-51	2-62
reflctns collected	4125	6824
reflctns used ($F > 3\sigma(F)$)	1711	3341
parameters refined	236	315
scan width, mm	0.85 + 0.35 tan θ	0.70 + 0.35 tan θ
$R(F) = \Sigma\|F_o - F_c\|/\Sigma\|F_o\|$	0.088	0.059
$R_w(F) = \Sigma\|F_o - F_c\|w^{1/2}/\Sigma\|F_o\|w^{1/2}$	0.096	0.057
$w = 1/(\sigma^2(F) + cF^2)$	$c = 0.024$	$c = 0.0005$
max shift error (non-H)	0.05	0.14
max shift/error (H)		0.39
res electron dens, e nm^{-3}	699	713

atoms. The coordinates of the hydrogen atoms were calculated following each refinement of the coordinates and thermal factors of the other atoms by the method of full-matrix least squares. The largest residual peaks (~700 e nm^{-3}) were near the iron atoms.

Meaningful refinement of the coordinates of the hydrogen atoms on the trimethylene bridge of IV was not possible because of the disorder of the central carbon atom of the bridge. Occupancies of 0.5 were assigned to the alternative positions of the disordered carbon atom. Refinement of the other hydrogen atoms and of all the non-hydrogen atoms was done by full-matrix least squares. The largest residual peaks (~700 e nm^{-3}) were near the iron atoms. Disorder of the central carbon atom of the bridge was not observed in III.

2,2′- and 3,3′-Difulvenyl-1,1′-trimethyleneferrocene (VII and VIII, Respectively). Sodium cyclopentadienide was prepared from 79 mL (63 g, 0.96 mol) of cyclopentadiene and 48 g (1.0 mol) of 50% NaH in mineral oil in 700 mL of THF in a three-neck flask equipped with a mechanical stirrer. DMS-DMF complex, prepared from 74 mL (70 g, 0.96 mol) of DMF and 91 mL (123 g, 0.98 mol) of DMS, was added to the solution of sodium cyclopentadienide with careful cooling in a dry ice–carbon tetrachloride bath. The product[28] 6-(dimethylamino)fulvene was obtained in 70% yield, 78 g (0.64 mol) based upon cyclopentadiene used.

In a typical preparation of VII and VIII a solution of 5.0 g (22 mmol) of III in 90 mL of hexanes was added to a solution of 5 mL of hexanes, 7 mL (5.4 g, 46 mmol) of TMEDA, and 21 mL (55 mmol) of 2.6 N *n*-butyllithium in a 250-mL three-neck flask equipped with a magnetic stirrer. Stirring at room temperature was continued for 2 days. The suspension of dilithio salt was transferred to a 500-mL three-neck flask equipped with a mechanical stirrer. A solution of 5.4 g (44 mmol) of 6-(dimethylamino)fulvene in 100 mL of THF was added rapidly with cooling in an ice-water bath. The red-black crude product obtained by workup according to an established procedure[15] contained a mixture of starting material, products that were presumed to be monosubstituted fulvenyltrimethyleneferrocenes but were not characterized, and VII and VIII. Repeated chromatography of the crude mixture was carried out with benzene–hexane mixtures under nitrogen pressure. The results following two successive chromatograms were 31% recovery of V, 14% yield of the presumed monosubstituted products,[16] 15% yield (1.26 g, 3.2 mmol) of VII, 16% yield (1.40 g, 3.6 mmol) of VIII, and 2% (0.2 g, 0.5 mmol) of a mixture of VII and VIII, accounting for 77% of the starting V. The high recovery of V was typical of these reactions and could not be attributed to a deficiency of *n*-butyllithium or to the presence of adventitious water. The products were unstable at room temperature (probably to polymerization) but could be stored for an undetermined time at −20 °C. They were characterized by their NMR spectra and by their further reaction to yield III and IV. Compound VII was recrystallized from a benzene–hexane mixture: mp 97–100 °C; NMR ($CDCl_3$) δ 6.0–6.1 and 6.3–6.5 (10 H, m, fulvenyl), 4.69 (2 H, t, 4, 4′), 4.26 (4 H, d, 3, 3′, 5, 5′), 1.88–2.25 (6 H, m, trimethylene CH_2). Compound VIII was recrystallized from a benzene–hexane mixture: mp 200 °C dec; NMR ($CDCl_3$) δ 5.95–6.10 and 6.25–6.65 (10 H, m, fulvenyl), 4.62 (4 H, d, 4, 4′, 5, 5′), 4.20 (2 H, t, 2, 2′), 1.95 (6 H, s, trimethylene CH_2).

2,2′-Trimethylene[1.1]ferrocenophane (III). To prepare $FeCl_2{\cdot}2THF$, a 250-mL round bottom flask containing 100–150 mL of THF was equipped with a 60-mL pressure-equalizing dropping funnel with a glass wool plug containing 2–7 g (16 to 55 mmol) of anhydrous $FeCl_2$ (Alfa Products). The dropping funnel was equipped with a reflux condenser, and the solution was heated at reflux overnight, the time required for most of the solid to be extracted. When the solution cooled, the solvent was decanted and 40 mL of THF was added to the white solid. The slurry was transferred to a Schlenk tube, and the $FeCl_2{\cdot}2THF$ was washed and dried as described,[16] or the slurry was used directly. In a typical preparation of III or IV, the $FeCl_2{\cdot}2THF$ was prepared from 1.9 g (15 mmol) of $FeCl_2$ by extraction with 125 mL of THF.

In a 1-L three-neck flask equipped with a magnetic stirrer, 30 mL of L-Selectride (Aldrich Chem. Co.) (30 mmol of lithium tri-*sec*-butylborohydride as a 1 M solution in THF) was added to 2.8 g (7.2 mmol) of VII. The dianion salt was transferred to a Schlenk tube as a slurry in 60 mL of hexanes, and the salt was washed as described.[16] The dianion salt was dissolved in 300 mL of THF and transferred to a 1-L pressure-equalizing dropping funnel. To 40 mL of THF was added the $FeCl_2{\cdot}2THF$ in hexanes, and the suspension was transferred to a 60-mL pressure-equilizing dropping funnel. The solid was kept in suspension by bubbling through nitrogen. The two suspensions were added dropwise to 400 mL of THF in the 1-L flask over a period of 15 min. Stirring was continued for 20 min. Workup was continued as described.[16] Filtration and extraction of the crude product prior to chromatography were accomplished in a Schlenk tube. Chromatography under nitrogen pressure on a vacuum-degassed alumina column (2.5 × 59 cm) with degassed CCl_4 yielded 0.767 g (24%) of III as the second band (the only major mobile band) with no impurity bands in the NMR spectrum. Recrystallization from toluene and methanol gave prismatic crystals: mp 224 °C dec; NMR (C_6D_6)

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δ 4.70 (2 H, m, 5, 5′), 4.44 (2 H, m, 10, 10′), 4.14 (2 H, t, $J = \sim 2.5$ Hz, 4, 4′), 4.03 (4 H, m, 8, 8′, 9, 9′), 3.95 (2 H, m, 3, 3′), 3.81 (2 H, m, 7, 7′), 3.32 (4 H, dd, J = 16–20 Hz, [1.1] CH_2), 1.25–2.15 (6 H, m, trimethylene CH_2).

3,3′-Trimethylene[1.1]ferrocenophane (IV). The same procedure was followed as for the preparation of III. In a typical experiment, 3.26 g (8.4 mmol) of VIII yielded 0.835 g (23%, maximum obtained was 29%) of IV. Recrystallization by vapor diffusion of hexanes into toluene gave gold leaflets: mp 218 °C dec; NMR (C_6H_6) δ 4.50 (2 H, m, 5, 5′), 4.21 (2 H, m, 10, 10′), 4.13 (4 H, m, 7, 7′, 9, 9′), 4.04 (2 H, m, 8, 8′), 3.88 (2 H, m, 2, 2′), 3.81 (2 H, m, 4, 4′), 3.32 (4 H, s, [1.1] CH_2), 1.81 (6 H, m, trimethylene CH_2).

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Supplementary Material Available: Tables of anisotropic thermal factors, isotropic thermal factors, and calculated and observed structure factors (24 pages). Ordering information is given on any current masthead page.

Reaction of SO_2 with Transition-Metal Hydrides. Synthesis and Structure of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-SO}_2)$

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The reaction of SO_2 with the unsaturated cluster $(\mu\text{-H})_2Os_3(CO)_{10}$ gives the adduct $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-SO}_2)$. Crystals of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-SO}_2)$ are monoclinic of space group $P2_1/n$ with lattice parameters at 203 K of a = 11.503 (2) Å, b = 12.357 (2) Å, c = 12.090 (3) Å, β = 89.51 (1)°, and Z = 4. The molecule consists of a triangular arrangment of osmium atoms with one nonbridged edge (Os–Os = 2.848 (1) Å), one edge bridged by a hydride (Os–Os = 3.068 (1) Å), and the third edge bridged by a hydride and the SO_2 (Os–Os = 2.895 (1) Å). The structure of the SO_2 complex is closely related to that of the methylene complex $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$.

Introduction

The reduction of SO_2 with hydrogen-containing compounds over heterogeneous catalysts is used in a number of industrial processes whose importance is certain to increase with increased use of fossil fuels. Although to date there has been only limited attention given to the reduction of SO_2 mediated by transition-metal complexes, it is likely that the study of such systems will lead to an enhanced understanding of the mechanistic aspects of SO_2 reduction and may indeed lead to homogeneous catalysts. Transition-metal complexes containing SO_2 and hydride ligands would be likely intermediates in the reduction process. Since the first hydrido SO_2 complexes were described by Levison and Robinson in 1972,[1] only two such compounds have been characterized by X-ray crystal structures[2,3] and rather few reactions of metal hydrides with SO_2 have been reported.[4-7]

Our recent investigations of the reactions between transition-metal hydride complexes and SO_2 have produced several new systems that show interesting reactivity. The reaction of SO_2 with $(\mu\text{-H})_2Os_3(CO)_{10}$ was chosen for study because this unsaturated cluster has been shown to form adducts with a considerable number of Lewis bases[8] and to transfer hydrogen to unsaturated ligands in certain cases.[9] In addition, new bonding modes have been observed for SO_2 in multimetal systems[10] and others are likely to be found. We report here on the initial adduct formed between SO_2 and $(\mu\text{-H})_2Os_3(CO)_{10}$.

Experimental Section

All preparations were carried out under a nitrogen or SO_2 atmosphere. Osmium carbonyl was purchased from Strem Chemicals, Newburyport, MA, and used to prepare $H_2Os_3(CO)_{10}$ by a published procedure.[11] Infrared spectra were recorded on

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