ORGANOMETALLICS

ansa-Metallocene derivatives. 26. Biphenyl-bridged metallocenes that are chiral, configurationally stable, and free of diastereomers

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Registry No. (R_P,R_P)-**1**, 143681-71-4; (S_P,R_P)-**1**, 143681-70-3; (S_P,S_P)-**1**, 143681-69-0; (R_P,R_P)-**2**, 143681-73-6; (S_P,R_P)-**2**, 143681-72-5; (S_P,S_P)-**2**, 143681-75-8; (R_P,R_P)-**3**, 143681-77-0; (S_P,R_P)-**3**, 143681-76-9; (S_P,S_P)-**3**, 143681-74-7; **5**, 37002-45-2; (R_P,R_P)-**6**, 143681-81-6; (R_P,S_P)-**6**, 143730-75-0; (S_P,S_P)-**6**, 143730-74-9; (R_P,R_P)-**7**, 143681-82-7; (R_P,S_P)-**7**, 143730-76-1; (S_P,S_P)-**7**, 143730-77-2; (R_P,R_P)-**8**, 143681-83-8; (R_P,R_P)-**8**·$0.5CH_2Cl_2$, 143681-84-9; (S_P,S_P)-**8**, 143730-78-3; (*R*,*R*)-DIOP, 32305-98-9; (*R*,*R*)-PAMPOP, 71359-99-4; DIPAMP, 97858-62-3; (*R*)-$CHNHAc(COOH)(CH_2Ph)$, 10172-89-1; (*S*)-$CHNHAc(COOH)(CH_2Ph)$, 2018-61-3; $PPh_2(2\text{-}MeOC_6H_4)$, 53111-20-9; $PPh(2\text{-}MeOC_6H_4)_2$, 36802-41-2; $PPh_2(4\text{-}MeOC_6H_4)$, 896-89-9; $PPh(2\text{-}Me_2NC_6H_4)_2$, 4551-07-9; $PPh_2(2\text{-}Me_2NC_6H_4)$, 4358-50-3; $MePPh_2$, 1486-28-8; $MePPh(2\text{-}MeOC_6H_4)$, 1485-88-7; $MePPh(4\text{-}MeOC_6H_4)$, 37042-93-6; $MeP(S)Ph(2\text{-}Me_2NC_6H_4)$, 143681-80-5; $MeP(O)Ph_2$, 2129-89-7; PhAc, 98-86-2; (*R*)-CHOH(Ph)(Me), 1517-69-7; (*S*)-CHOH(Ph)(Me), 1445-91-6; $Ph_2C{=}NCH_2COOMe$, 81167-39-7; (*R*)-$Ph_2C{=}NCH(COOMe)(CH_2CH{=}CH_2)$, 118169-13-4; (*S*)-$Ph_2C{=}NCH(COOMe)(CH_2CH{=}CH_2)$, 118169-12-3; $Pd(OAc)_2$, 3375-31-3; Ph_2SiH_2, 775-12-2; $C_6H_4O_2BH$, 274-07-7; potassium (2-methoxyphenyl)phenylphosphide, 143681-85-0; molybdenum tetracarbonyl, 44780-98-5; (2-(dimethylamino)phenyl)phenylphosphide, 143681-78-1; (2,6-bis(methoxy)phenyl)phenylphosphide, 143681-79-2; chloro(1,5-cyclooctadiene)rhodium(1+) dimer, 12092-47-6; acetamidocinnamic acid, 5469-45-4; norbornene, 498-66-8; indene, 95-13-6; styrene, 100-42-5; (*R*)-*exo*-norborneol, 29583-34-4; (*S*)-1-indanol, 25501-32-0; allyl acetate, 591-87-7.

Supplementary Material Available: Tables of atomic coordinates, anisotropic displacement parameters, hydrogen atom positional parameters, and bond angles and distances and diagrams showing the atom-labeling and numbering system for (R_P,R_P)-**6**, (R_P,R_P)-**7**·CH_2Cl_2, (R_P,R_P)-**8**, and (S_P,S_P)-**8** (85 pages). Ordering information is given on any current masthead page.

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Biphenyl-Bridged Metallocenes That Are Chiral, Configurationally Stable, and Free of Diastereomers[1]

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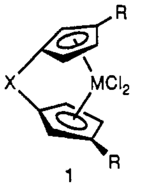
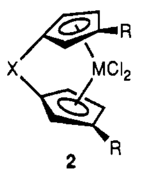
Formation of diastereomers is precluded when biphenyl-bridged bis(cyclopentadienyls) and transition-metal halides combine to give chiral *ansa*-metallocenes. These cyclopentadienyls must be symmetrically substituted. Syntheses and X-ray diffraction analyses are reported for four biphenyl-bridged *ansa*-metallocenes: titanocene dichlorides **17** and **22**, zirconocene dichloride **18**, and ferrocene **13**.

Introduction

Bridged chiral metallocenes—**1** for example—are the basis of reagents and catalysts that bring about a number of transformations stereoselectively.[2] However, syntheses of these metallocenes are commonly encumbered by formation of their meso isomers **2**.[3] In only one case did the desired racemic structure predominate overwhelmingly,[3i,4] but even then not when the procedure was altered in a seemingly minor way.[3j] A design would, therefore, be desirable that would eliminate the meso isomers. A strategy that Halterman,[5] McLaughlin,[6] and Bosnich[7] used to achieve this goal is to connect chiral groups to the precursors in order to increase the forces favoring one diastereomer. An alternative, which we report here, is to



1
racemic



2
meso

M = Ti, Zr
X = Me_2Si, Me_4C_2

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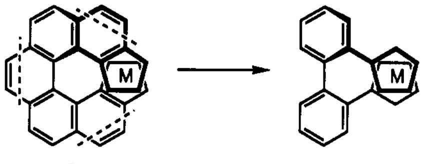
create structures that can not possibly give meso forms. In fact, there is already one class of chiral metallocenes for which this desideratum is fulfilled, the helicene sandwich compounds **3**.[8] In these, diastereoisomerism could occur only if many bonds were unreasonably distorted. We have now truncated such helicenes to their minimal essentials, biphenyls bridging two cyclopentadienyl rings (**4**), and we have demonstrated that such simplified ligands give metallocenes with the following characteristics: (i) diastereomers cannot arise as long as the cyclopentadienyl rings are symmetrically substituted; (ii) racemization is prevented by the rigidity of the biphenyl bridge; (iii) unlike *ansa*-metallocenes with flexible alkano bridges, the two β-positions at each C_5 ring are therefore inequivalent.



3 **4**

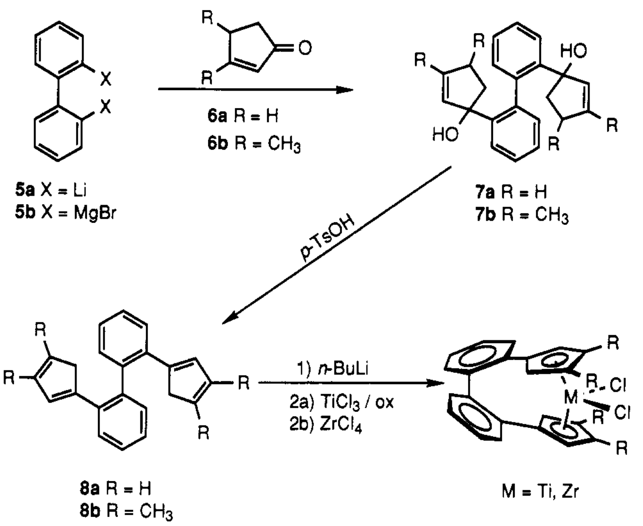
This means that derivatives of **4** must retain their chirality at normal temperatures even when their cyclopentadienyl rings carry identical substituents at both β-positions. Substituents in these positions should enhance the enantiofacial selectivity experienced by prochiral substrates bound to the metal centers. As we see below, these substituents confer an immediate benefit. They facilitate the linkage of the biphenyl and cyclopentadienyl moieties.

Results

The plan (Scheme I) was to react 2,2′-dilithiobiphenyl (**5a**) or 2,2′-bis(bromomagnesio)biphenyl (**5b**) with cyclopent-2-en-1-one (**6a**). Dehydration of the resulting bis(cyclopentenol) **7a** with mild acid should give the bis(cyclopentadiene) **8a**, which when deprotonated by 2 mol of *n*-BuLi and reacted with $TiCl_3$ (then HCl in air) or $ZrCl_4$ should give the racemic *ansa*-metallocenes.

2,2′-Dibromobiphenyl was, therefore, converted to its dilithium salt (**5a**), by reaction with *n*-BuLi, and combined with cyclopent-2-en-1-one (**6a**) in THF at −70 °C. The product, however, was a complex mixture of 1,2- and 1,4-adducts of the aryllithium to the cyclopentenone, as well as biphenyl, the latter presumably forming when the cyclopentenone enolizes. The IR spectrum of the crude product displayed strong absorption at 1735 cm^{-1}, characteristic of cyclopentanones (1,4-adducts), and much smaller absorptions at 3500 and 3050 cm^{-1}, characteristic of alcohols and vinyl C–H's (1,2-adducts). In some experiments biphenyl was isolated by flash chromatography on silica gel, while in others it was identified by its characteristic ^{1}H NMR peaks at δ 7.38 (m, 6 H) and 7.60 (d, 2 H). Flash chromatography failed to give any of the bis(cyclopentenol) **7a**. Dehydration of the mixture under mildly acidic (*p*-TsOH, benzene) or basic conditions (MsCl, pyridine or Tf_2O, 2,6-lutidine) gave polymeric materials and none of the desired bis(cyclopentadiene) **8a**. In similar experiments using **5a** and **5b** in the presence of $CeCl_3$[9] or $La(OTf)_3$,[10] neither the ratio of 1,2- to 1,4-adducts increased nor the amount of biphenyl decreased. When 2-methyl-2-cyclopentenone was used in place of cyclopent-2-en-1-one **6a**, the results were similar.

Scheme I



However, when 3,4-dimethylcyclopent-2-en-1-one (**6b**)[11] was used instead, the coupling with biphenyl was successful. Thus, when 2 mol of the ketone was allowed to react in ether at −70 °C with 2,2′-dilithiobiphenyl, a solid was obtained, which upon hydrolysis gave a yellow oil. TLC analysis showed **6b** and biphenyl, probably reflecting enolization of the ketone by 2,2′-dilithiobiphenyl, plus four new spots. The new products are possibly the three diastereomeric forms of the bis(cyclopentenol) **7b** and the monoadduct **14**. Evidence that **7b** and **14** are present will be seen below. However, although present, the desired bis(cyclopentenol) **7b** could not be isolated and purified either by crystallization or by chromatography on silica gel.

Alternative methods, such as $TiCl_4$-mediated reactions of 2,2′-dilithiobiphenyl (**5a**) with **6b**[12] and Pd-catalyzed cross-coupling of 2,2′-diiodobiphenyl with the ethylene ketal of 2-(ZnCl)-cyclopent-2-en-1-one,[13] did not couple the biphenyl and cyclopentadienyl structures. However, a palladium-catalyzed coupling with ferrocene did (Scheme II). It was based on the demonstration by Rosenblum et al. that Pd catalysts unite ferrocenylzinc chlorides with 1,8-diiodonaphthalene, giving good to excellent yields, of ferrocene–naphthalene oligomers.[14] If the iron atoms could then be removed by reduction, the desired bis(cyclopentadiene) **8a** would be produced.[15] Lithioferrocene was synthesized either from bromoferrocene[16] or more conveniently from ferrocene,[17] and it was converted to the corresponding zinc chloride species **9**. Reaction of **9** with 2,2′-diiodobiphenyl in the presence of $Pd(PPh_3)_2$, synthesized by reducing $(Ph_3P)_2PdCl_2$ with 2 mol of Dibal in THF,[14] gave a good yield of 2,2′-diferrocenylbiphenyl (**10**),

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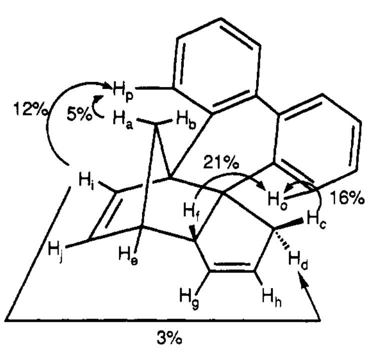
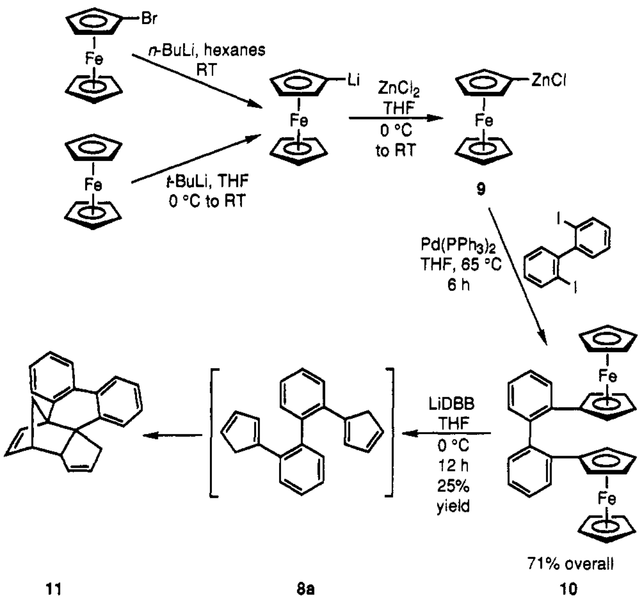


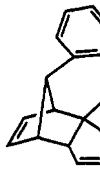
Figure 1. Significant NOE's in 11.

Scheme II

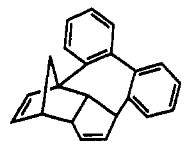


an orange solid. However, attempts to reduce 10 with 5 mol of Li in $EtNH_2$, conditions that quickly reduce ferrocene to lithium cyclopentadienide and Fe^0,[18] only returned starting material. The results with other reducing agents (Li in NH_3, −78 to −35 °C; lithium naphthalenide, THF, 0 °C; sodium naphthalenide, THF, 0 °C) were similar. Lithium di-*tert*-butylbiphenylide (LiDBB)[19] does bring about the reduction, but the product it gives in moderate yield is not the desired bis(cyclopentadiene) 8a. It is instead the intramolecular Diels–Alder adduct 11. The source of the protons that produce 8a is not known, and attempts to trap 8a with excess KO-*t*-Bu or LiDBB or the corresponding dianion with $TiCl_3(THF)_3$[20] or $[Cp^*CoCl]_2$[21] prior to aqueous workup failed.

Structure of 11. The structure of 11 was analyzed by MS, ^1H NMR, ^{13}C NMR, NOE-difference spectroscopy, and COSY. The MS (CI, CH_4) shows the required strong M + 1 peak at m/z 283. The intensities and chemical shifts in the ^1H NMR spectrum do not agree with the bis(cyclopentadiene) structure 8a (^1H NMR for cyclopentadiene: δ 2.90 (2 H) and 6.42 (4 H).[22] In addition, strongly coupled resonances at δ 1.56 and 1.81 are similar to two in dicyclopentadiene, at δ 1.27 and 1.45.[23] The shifts of the resonances downfield in 11 may be due to deshielding by the biphenyl. The way the biphenyl and the dicyclopentadiene are connected is revealed by the ^{13}C NMR spectrum, which shows two quaternary signals, at δ 59.2 and 55.1, assigned to the bridgehead carbons of the dicyclopentadiene structure.[23] Other plausible structures (**11a,b**) cannot account for these two resonances.



11a

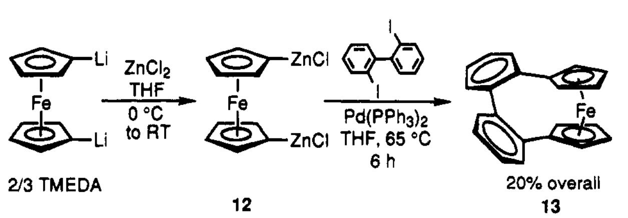


11b

NOE difference spectroscopy (Figure 1) confirms the structure proposed. The strong NOE's between H_f and H_o (21%) and H_c and H_o (16%), as well as the 3% NOE between H_i and H_d, imply that 11 is an endo dicyclopentadiene. If the structure were **11b**, the NOE between H_f and H_o would be expected to be much smaller. If the structure were **11a**, the NOE between H_i and H_p would be absent and a moderate NOE between H_e and H_p, which is not seen, should have been observed. A complete list of proton assignments and NOE's is presented in the supplementary material. For this analysis, COSY was used to assign the aromatic proton resonances. In addition, COSY revealed the long-range W coupling between H_f and H_d normally seen in dicyclopentadienes.[23]

Heating 11 in refluxing decalin over NaH, cooling to 0 °C, adding a solution of $TiCl_3(THF)_3$ in THF, refluxing the resulting mixture, and oxidizing with 6 M HCl in air at room temperature failed to give any bridged metallocene and returned 36% of 11. Rosenblum et al. applied similar conditions to a naphthalene–dicyclopentadiene to synthesize a bridged 1,8-naphthalenediylferrocene.[24] Reducing 11 with LiDBB in THF, adding a solution of $TiCl_3(THF)_3$ in THF, refluxing, and oxidizing at room temperature with 6 M HCl in air also failed to give the expected titanocene. It gave no Diels–Alder adduct 11 either!

Synthesis of a Bridged *ansa*-Ferrocene. The formation of a biphenyl-bridged *ansa*-metallocene was finally realized when the zinc chloride salt 12 of dilithioferrocene/TMEDA[14] was combined with 2,2′-diiodobiphenyl[25] in the presence of 5 mol % $Pd(PPh_3)_2$. This gives in 20% yield an orange solid whose ^1H NMR, ^{13}C NMR, MS, IR, and elemental analysis are consistent with 13, a biphenyl-bridged *ansa*-ferrocene (eq 1). Accompanying



(1)

this product are large amounts of oligomers of ferrocene and 2,2′-biphenyl. However, unlike 1,8-diiodonaphthalene, whose analogous reaction gives only oligomers,[14] the diiodobiphenyl gives the bridged ferrocene as well. The

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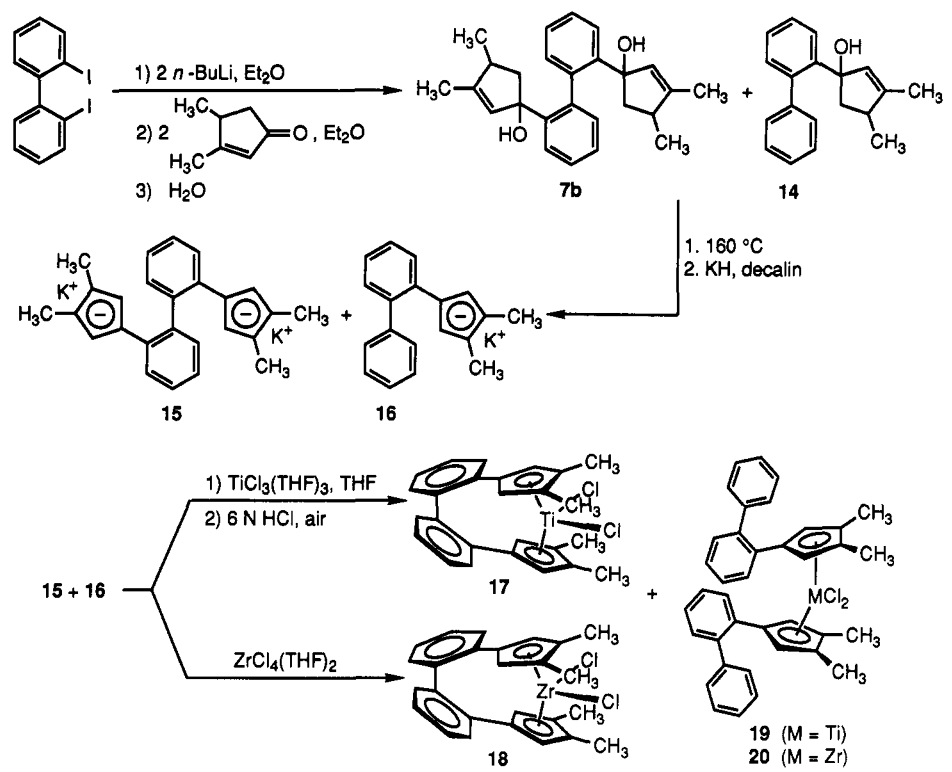
Scheme III



greater flexibility of the biphenyl may be the reason.

The structure of *ansa*-ferrocene **13**, determined by an X-ray analysis of crystals grown by slowly evaporating a concentrated benzene solution at room temperature, is shown in Figure 2.

Syntheses of Bridged *ansa*-Titanocene and Zirconocene Dichlorides. The method used to synthesize **13** could not be extended to synthesize *ansa*-metallocenes of group IV metals because appropriate dihalo group IV metallocenes are unavailable. They are not described in the chemical literature, and attempts to synthesize them failed. For this reason, we returned to the reaction that produced **7b** and used the crude mixture of alcohols without further purification (Scheme III). Thermal dehydration of these alcohols at 160 °C[26] proceeded quantitatively within less than 2 h.[27] To minimize polymerization, the resulting oily product was immediately deprotonated without purification.

When this was done with excess *n*-BuLi in hexane at room temperature, subsequent reaction with $TiCl_3(THF)_3$ followed by oxidation with HCl in air did not lead to the desired biphenyl-bridged titanocene **17**. It gave instead an unbridged compound, possibly **19**.[28] An analogous sequence, carried out in refluxing hexane, yielded a mixture of this compound and **17** in a ratio of 6:1 (^1H NMR analysis). Perhaps some, but not much, **17** is obtained because the bis(cyclopentadiene) **8b** undergoes an intramolecular Diels–Alder reaction (such as the one described above), whose product cracks partially when it is in hexane that is boiling, but not in hexane at room temperature.

In the higher boiling decalin, at reflux with excess KH, the method of Rosenblum,[24] the dehydration product of diol **7b** produces a dark brown tarry solid, which was reacted with $TiCl_3(THF)_3$ in THF (Scheme III). The resulting black solution when oxidized with 6 M HCl in the presence of air turns red immediately. From this solution dark red crystals separate upon standing at 0 °C. The remaining product was purified by eluting it from a short column of silica gel with pentane/Et_2O (10:1). In this way an 18% yield[29] of the biphenyl-bridged titanocene dichloride **17** was obtained (Scheme III). There was no contamination by unbridged materials, such as **19**.

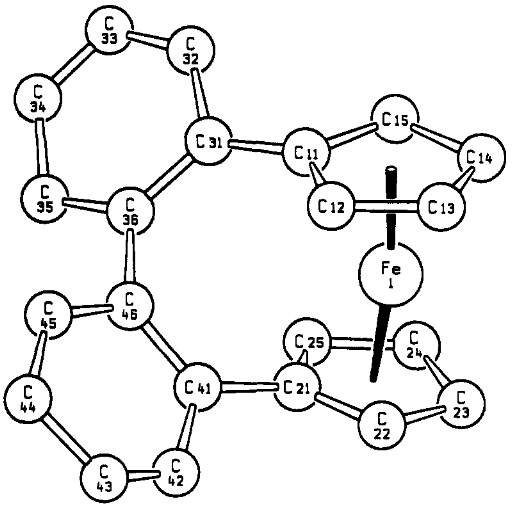


Figure 2. Structure of **13** as analyzed by X-ray diffraction.

The corresponding zirconocene dichloride was obtained similarly when the transition-metal salt was $ZrCl_4(THF)_2$[20] in THF (Scheme III). The crude product consisted of material that is probably the unbridged **20**[30] and the bridged **18** in a ratio of 1:3 (^1H NMR analysis). The latter

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[26] Riemschneider, R.; Nerin, R. *Monatsh. Chem.* **1960**, *91*, 829.

[27] TLC analysis showed that the four spots attributed to **7b** and **14** disappeared and a new fast-moving spot appeared.

[28] A *sharp singlet* in the ^1H NMR spectrum at δ 5.51 is attributed to this structure. The purified analogue that has four methylenes in place of the two methyls displays a sharp singlet at δ 5.56 (Huttenloch, M., unpublished results).

[29] The yield is based on 2,2′-diiodobiphenyl.

[30] A *sharp singlet* in the ^1H NMR spectrum at δ 5.50 is attributed to this structure.[28]

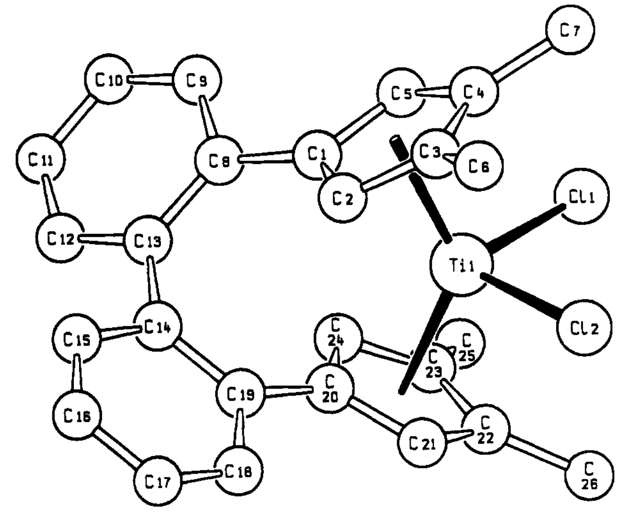


Figure 3. Structure of **17** as analyzed by X-ray diffraction.

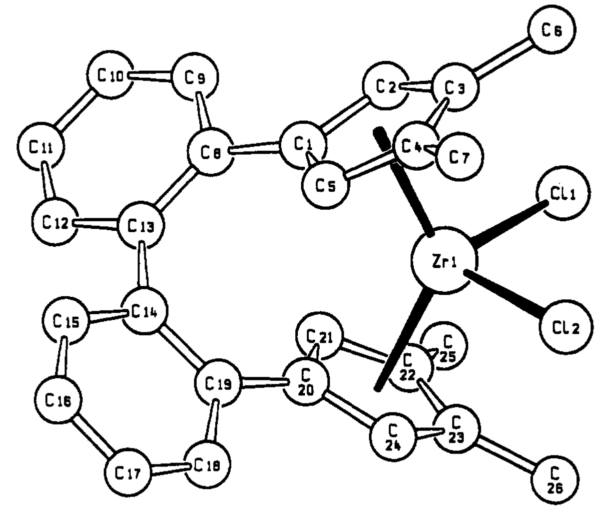
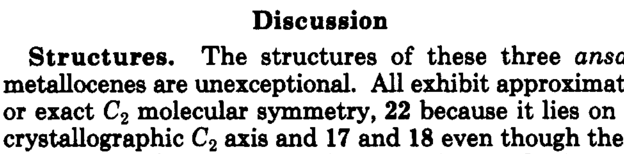


Figure 4. Structure of **18** as analyzed by X-ray diffraction.

could be extracted with hot hexane and recrystallized from Et_2O/hexane (4:1). This gave **18** as yellow plates in 3% yield.[29] This procedure has also been used to prepare *ansa*-titanocene **22** (eq 2) in 4% yield from 2,2′-diido-6,6′-dimethylbiphenyl (**21**).[31]



(2)

21 **22**

The structures of **17**, **18**, and **22**, analyzed by X-ray diffraction, are represented in Figures 3–5, and relevant features are summarized in Table I.

Discussion

Structures. The structures of these three *ansa*-metallocenes are unexceptional. All exhibit approximate or exact C_2 molecular symmetry, **22** because it lies on a crystallographic C_2 axis and **17** and **18** even though they do not. The dihedral angles between the two C_5 rings in each complex are all approximately 52°. These and the cyclopentadienyl centroid–metal–cyclopentadienyl centroid angles (131.1–134.0°) and Cl–metal–Cl angles (94.5–96.5°) are all similar to angles found in normal, unbridged group IV metallocene dichlorides.[32] Compared to other bridges,[3a,b,h,i,33] the biphenyl appears to diminish the Cp–M–Cp angles less from the values commonly seen in related unbridged metallocene dihalides.[32] Notable, however, are the conformations of the C_5 rings. Because the span of the biphenyl bridge is so large, one of the β-substituents on each cyclopentadienyl is close to the plane that bisects

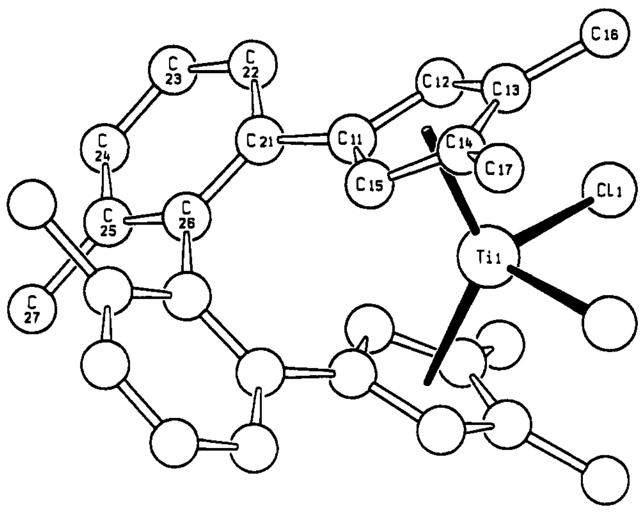


Figure 5. Structure of **22** as analyzed by X-ray diffraction.

Table I. Selected Distances (pm) and Angles (deg) for the Biphenyl-Bridged Metallocene Complexes 17, 18, and 22

	17 (M = Ti)	18 (M = Zr)	22 (M = Ti)[d]
M(1)–Cl(1)	234.3 (1)	242.2 (1)	234.8 (3)
M(1)–Cl(2)	234.3 (1)	244.2 (1)	
M(1)–C(1)	239.2 (3)	249.2 (4)	238.2 (9)
M(1)–C(2)	236.8 (3)	249.4 (4)	236.6 (10)
M(1)–C(3)	248.8 (3)	255.7 (4)	245.7 (11)
M(1)–C(4)	246.4 (3)	259.3 (4)	249.2 (8)
M(1)–C(5)	238.1 (3)	249.7 (4)	238.2 (8)
M(1)–C(20)	236.9 (3)	251.1 (4)	
M(1)–C(21)	237.9 (3)	250.3 (4)	
M(1)–C(22)	245.1 (3)	257.5 (4)	
M(1)–C(23)	247.4 (3)	254.8 (4)	
M(1)–C(24)	236.8 (3)	248.7 (4)	
M(1)–CR(1)[a]	210.0	222.5	210
M(1)–CR(2)	208.7	222.1	
Cl(1)–M(1)–Cl(2)	94.5 (1)	96.5 (1)	94.6 (1)
CR(1)–M(1)–CR(2)	133.1	131.5	134.0
CP(1)–CP(2)[b]	52.9	52.7	51.7
PH(1)–PH(2)[c]	55.9	57.9	70.2
PH(1)–CP(1)	24.4	22.4	19.1
PH(2)–CP(2)	17.0	24.2	

[a] CR(1), CR(2) = centroids of C atoms numbered 1–5 and 20–24, respectively. [b] CP(1), CP(2) = mean planes of corresponding C_5 rings. [c] PH(1), PH(2) = mean planes of C_6 rings attached to CP(1) and CP(2). [d] Add 10 to the numbering of each C atom listed in column 1; distances and angles not listed are identical with those of their C_2-symmetry-related counterparts.

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(31) Mislow, K.; Glass, M. A. W.; O'Brien, R. E.; Rutkin, P.; Steinberg, D. H.; Weiss, J.; Djerassi, C. *J. Am. Chem. Soc.* **1962**, *84*, 1455.

(32) (a) Clearfield, A.; Warner, D. K.; Saldarriaga-Molina, C. H.; Ropal, R.; Bernal, I. *Can. J. Chem.* **1975**, *53*, 1622. (b) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422. (c) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2290. (d) Rogers, R. D.; Benning, M. M.; Kurihara, L. K.; Moriarty, K. J.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *293*, 51. (e) Howie, R. A.; McQuillan, G. P.; Thompson, D. W.; Lock, G. A. *J. Organomet. Chem.* **1986**, *303*, 213. (f) Antiñolo, A.; Lappert. M. F.; Singh, A.; Winterborn, D. J. W.; Englehardt, L. M.; Raston, C. L.; White, A. H.; Carty, A. J.; Taylor, N. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1463.

(33) (a) Bajgur, C. S.; Tikkanen, W. R.; Petersen, J. L. *Inorg. Chem.* **1985**, *24*, 2539. (b) Köpf, H.; Pickhardt, J. *Z. Naturforsch., B* **1981**, *36B*, 1208.

Table II. Crystallographic and Experimental Data for Complexes $C_{26}H_{24}Cl_2Ti$ (17), $C_{26}H_{24}Cl_2Zr$ (18), and $C_{28}H_{28}Cl_2Ti$ (22)

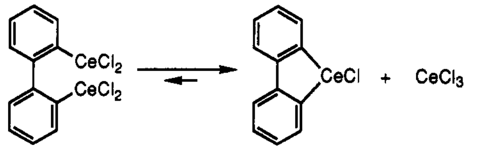
	17	18	22
formula	$C_{26}H_{24}Cl_2Ti$	$C_{26}H_{24}Cl_2Zr$	$C_{28}H_{28}Cl_2Ti$
fw	455.3	498.6	483.3
cryst color, form	red cube	yellow plate	red needle
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2/a$ (No. 13)
a, pm	1492.34 (4)	1115.1 (3)	1558.0 (3)
b pm	902.2 (2)	1371.2 (3)	1102.2 (2)
c, pm	1644.1 (4)	1492.9 (4)	1560.0 (2)
β, deg	93.14 (2)	102.76 (2)	116.97 (1)
V, 10^6 pm^3	2210.1 (1)	2226.4 (10)	2387.5 (6)
d_{calcd}, g/cm^3	1.37	1.49	1.34
Z	4	4	4
cryst dimens, mm	0.5 × 0.5 × 0.5	0.2 × 0.1 × 0.1	0.2 × 0.2 × 0.7
abs coeff (μ), cm^{-1}	6.36	7.37	6.1
T, K	296	296	298
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0004F^2$	$w^{-1} = \sigma^2(F) + 0.0002F^2$	$w^{-1} = \sigma^2(F) + 0.00074F^2$
scan mode	Wyckoff	Wyckoff	Wyckoff
2θ range, deg	4.0–54.0	4.0–54.0	3.0–45
scan speed, deg/min	2.3–29.3	2.3–29.3	4.0–29.3
no. of rflns measd	5328	5343	3456
no. of data used	4816	4871	1690
obseron criterion	$F > 4.0\sigma(F)$	$F > 6.0\sigma(F)$	$F > 6.0\sigma(F)$
no. of params varied	262	262	282
R_F[a]	0.046	0.035	0.052
R_{wF}[b]	0.054	0.038	0.071
residual density, 10^{-6} e pm^{-3}	0.35	0.42	0.40

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_c\delta|$. [b] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum F_o^2]^{1/2}$.

the Cl–metal–Cl angle.[34] It is also interesting that, presumably to diminish steric interactions between them, the methyls on the biphenyl that distinguish structure **22** from structure **17** increase the angle between the biphenyl's planes.

Each of the four structures clearly shows the inequivalence of the two β-positions at the C_5 rings. Separate ^1H NMR signals for the β-H atoms in **13** and for the β-CH_3 groups in **17**, **18**, and **22** demonstrate that these complexes are configurationally stable on the NMR time scale. Experiments are in progress to further establish their thermal and photochemically stability, which is likely to be increased by the extra methyl substituents in **22**.

Syntheses. The synthesis of ligand **8a** proved much more difficult than expected. It was surprising that 2,2′-dilithiobiphenyl (**5b**), instead of adding to the carbonyl of cyclopent-2-en-1-one (**2a**), the way aryllithiums usually add to enones,[35] added primarily to the 4-position and enolized the ketone as well. Possibly steric hindrance in the aryllithium is to blame. Also surprising was that the addition of **5b** to **6a** proceeded predominantly by 1,4-addition even in the presence of $CeCl_3$, for such combinations are known to lead to carbonyl adducts.[9] Maybe 2,2′-bis(dichlorocerio)biphenyl (**23**) disproportionates to 2,2′-biphenyldiylcerium chloride (**24**) and cerium trichloride, and the chemistry observed is that of **24** (eq 3). This suggests that if excess $CeCl_3$ were added to the reaction mixture, the ratio of 1,4- to 1,2-adduct would decrease, but experiments failed to confirm the idea. Lanthanum triflates and $TiCl_4$ gave similar disappointing results.



23 **24** (3)

One solution to the problem is not to synthesize **8a** but instead (as in eq 1) to couple a preformed metallocene to a biphenyl. Another is to use, in place of cyclopentenone, 3,4-dimethylcyclopent-2-en-1-one (**6b**). The success with this ketone implies that methyl substituents at the 3- and 4-positions in **6b** slow the normal rate of 1,4-addition and thereby enhance the amount of 1,2-addition that takes place. The essential point is that these substituents make possible the synthesis of the racemic bridged *ansa*-titanocene and zirconocene dichlorides, while the biphenyl bridge prevents meso isomers from forming at the same time.

Experimental Section

General Information. The atmosphere under which reagents were combined was argon. Diethyl ether and tetrahydrofuran were distilled under argon from sodium or potassium benzophenone ketyl. Decalin and hexane were distilled under argon from $LiAlH_4$. *t*-BuLi/pentane was titrated against *l*-menthol in xylenes, with 1,10-phenanthroline as an indicator.[36] Preparative silica gel (Woelm 32–62, 32–63 μm) column chromatography was conducted according to the method of Still.[37] The plates used for thin-layer chromatography (TLC) were E. Merck's silica gel 60 F-254 (0.25-mm thickness), precoated on glass, and they were visualized under both long- (365 nm) and short-wavelength (254 nm) UV light.

Crystal Structure Determinations. The instruments used to determine the structures were four-circle diffractometers, a Syntex/Siemens-P3 for **17** and **18** and a Nicolet R3m for **13** and **20**. Table II summarizes the crystal data. Other data are recorded in the supplementary material.

2,2-Diferrocenylbiphenyl (10). To 9.03 g (49 mmol) of ferrocene in 40 mL of THF at −78 °C was added 22.1 mL (41 mmol) of a 1.83 M solution of *t*-BuLi/pentane. The resulting orange slurry was stirred at 0 °C for 15 min and at room temperature for 1 h. The resulting lithioferrocene[17] was transferred via a cannula into a solution of 4.78 g (35 mmol) of $ZnCl_2$ in 40 mL of THF at 0 °C, contained in a 200-mL three-necked round-bottomed flask equipped with a water-cooled reflux con-

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[34] Practically identical conformations were recently observed in zirconocene complexes that contain disubstituted C_5-ring ligands and are doubly bridged by two dimethylsilyl groups (Mengele, W.; Diebold, J.; Troll, C.; Röll, W.; Brintzinger, H. H., unpublished results).

[35] Gilman, H.; Kirby, R. H. *J. Am. Chem. Soc.* **1941**, *63*, 2046.

[36] Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

[37] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

denser and a pressure-equalizing addition funnel. The resulting orange solution was warmed to room temperature for 1 h to give ferrocenylzinc chloride (**9**). In a separate flask, 260 mg (0.37 mmol) of $(Ph_3P)_2PdCl_2$ and 10 mL of THF were combined to give a yellow slurry, to which at room temperature was added dropwise 0.74 mL (0.74 mmol) of a 1.0 M solution of Dibal/hexanes. This gave a homogeneous dark solution of $(Ph_3P)_2Pd$.[14] The Pd catalyst was added to the ferrocenylzinc chloride via a cannula. 2,2′-Diiodobiphenyl[25] (3.0 g, 7.4 mmol) in 30 mL of THF was added dropwise through the addition funnel during the course of 30 min, and the resulting dark solution was brought to reflux for 6 h. The reaction mixture was cooled to room temperature, carefully quenched by adding 20 mL of brine, and extracted with 2 × 100 mL of CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$, filtered, and evaporated to give an orange solid. Flash chromatography on silica gel using hexanes, 10/1 hexanes/CH_2Cl_2, and finally 3/1 hexanes/CH_2Cl_2 yielded 2.74 g (5.25 mmol, 71% yield) of **10**, an orange solid (TLC: R_f 0.16, 3/1 hexanes/CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.05 (s, 14 H), 4.11 (m, 4 H), 6.95 (dd, 2 H), 7.13 (td, 2 H), 7.31 (td, 2 H), 7.78 (dd, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 67.89, 67.92, 69.5, 69.7, 69.8, 85.4, 125.3, 126.7, 129.9, 130.6, 137.6, 140.5. MS (CI, CH_4): *m/z* 523 (M = 1, 100%), 457 (M = C_5H_4, 30%), 337 (M = $C_{10}H_9Fe$, 100%). Experiments in which lithioferrocene was prepared from bromoferrocene and *n*-BuLi[16b] gave similar results.

2,2′-Dicyclopentadienylbiphenyl 11. A deep green-blue solution of LiDBB[19] was prepared by adding 18 mg (2.64 mmol) of clean, flattened lithium wire to a solution of 839 mg (2.93 mmol) of 4,4′-di-*tert*-butylbiphenyl in 30 mL of THF and stirring with a Pyrex-enclosed magnetic stirring bar at 0 °C. The formation of LiDBB was deemed complete when no more lithium wire was visible in the solution (6 h). To this solution at 0 °C was added 300 mg (0.58 mmol) of 2,2′-diferrocenylbiphenyl (**10**) in 30 mL of THF, in drops via cannula. The resulting mixture was stirred at 0 °C for 10 h. The reaction mixture was quenched by adding 10 mL of brine and extracted with 2 × 50 mL of pentane. The combined organic extracts were dried over $MgSO_4$, filtered, and evaporated, giving a light orange solid. Flash chromatography on silica gel using 10/1 hexanes/CH_2Cl_2 followed by 3/1 hexanes/CH_2Cl_2 yielded 42 mg (0.15 mmol, 25% yield) of **11**, a white solid (TLC: R_f 0.44, 3/1 hexanes/CH_2Cl_2). ^{1}H NMR (400 MHz, C_6D_6): δ 1.56 (d, 1 H), 1.81 (d, 1 H), 2.02 (dd, 1 H), 2.19 (dd, 1 H), 2.62 (m, 1 H), 3.62 (m, 1 H), 5.39 (m, 1 H), 5.62 (m, 1 H), 6.17 (m, 2 H), 7.14 (m, 2 H), 7.19 (m, 2 H), 7.30 (m, 1 H), 7.50 (m, 1 H), 7.76 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 44.8, 45.8, 55.1, 55.8, 59.2, 68.6, 123.0, 123.6, 126.1, 127.7, 127.8, 128.3, 128.4, 130.4, 131.4, 132.1, 133.1, 136.4, 137.8, 137.9, 147.0. MS (CI, CH_4): *m/z* 283 (M + 1, 100%), 311 (M + 29, 25%), 217 (M − C_5H_5, 20%).

2,2′-(1,1′-Ferrocenediyl)biphenyl (13). To a solution at 0 °C of 300 mg (2.2 mmol) of anhydrous $ZnCl_2$ in 10 mL of THF in a 100-mL three-necked round-bottomed flask equipped with a water-cooled reflux condenser and pressure-equalizing addition funnel was added a slurry of 606 mg (2.2 mmol) of 1,1′-dilithioferrocene/TMEDA complex[14] in 15 mL of THF via cannula. The resulting orange slurry of **12** was warmed to room temperature and stirred for 1 h. In a separate flask, 77 mg (0.11 mmol) of $(Ph_3P)_2PdCl_2$ and 5 mL of THF were combined to give a yellow slurry. To this slurry at room temperature was added dropwise 0.22 mL (0.22 mmol) of a 1.0 M solution of Dibal/hexanes. This gave a homogeneous dark solution of $(Ph_3P)_2Pd$.[14] The Pd catalyst was added via cannula to the ferrocenylzinc chloride slurry, and the resulting brown/black mixture was heated to reflux. 2,2′-Diiodobiphenyl[25] (894 mg, 2.2 mmol) in 15 mL of THF was added dropwise from the addition funnel over 1 h, and the resulting black solution was refluxed for 12 h. After it had been cooled to room temperature, the reaction mixture was quenched with 20 mL of brine and extracted with 2 × 50 mL of CH_2Cl_2. The combined organic layers when dried over $MgSO_4$, filtered, and evaporated gave a light orange solid. Flash chromatography on silica gel, with 10/1 hexanes/CH_2Cl_2 and 5/1 hexanes/CH_2Cl_2 as eluent, yielded 147 mg (0.44 mmol, 20%) of **13**, an orange solid (TLC: R_f 0.50, 1/1 hexanes/CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.67 (d, 2 H), 4.09 (d, 2 H), 4.39 (d, 2 H), 4.50 (d, 2 H), 7.20–7.40 (m, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$: δ 67.2, 69.2, 73.6, 76.7, 82.3, 126.7, 127.2, 127.4, 133.6, 137.2, 140.4. MS (EI): *m/z* 336 (M^+, 100%). Anal. Calcd for $C_{22}H_{16}Fe$: C, 78.59; H, 4.80. Found: C, 78.84; H, 4.87. Analysis by X-ray crystallography shows the structure to be **13**, but the *R* factor (15.5%) was so large that detailed bond angles and lengths cannot be stated with confidence. The crystals are monoclinic, $P2_1/_c$, with a = 11.563 (6) Å, b = 9.756 (2) Å, c = 27.620 (9) Å, β = 99.40 (4)°, V = 3073 (2) Å, and Z = 8. Continued elution with CH_2Cl_2 and Et_2O yielded ferrocene–2,2′-biphenyl oligomers.

Synthesis and Deprotonation of 2,2′-Bis(3,4-dimethylcyclopentadienyl)biphenyl (8b). 2,2′-Dilithiobiphenyl was prepared in situ by adding 17 mL (27 mmol) of a 1.6 M solution of *n*-BuLi/hexane at −70 °C to 5.5 g (13.5 mmol) of 2,2′-diiodobiphenyl in 60 mL of Et_2O. The reaction mixture was stirred for 30 min at −70 °C and for 3 h at room temperature. The resulting yellow solution was cooled to −70 °C, and 3 g (27 mmol) of 3,4-dimethylcyclopent-2-en-1-one (**6b**)[11] in 30 mL of Et_2O was added dropwise. After it had been stirred for 1 h at −70 °C and 6 h at room temperature, the mixture was hydrolyzed with ice water and extracted twice with 2 × 100 mL of Et_2O. The combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure. The remaining yellow oil was transferred into a Schlenk vessel and dehydrated without further purification by heating it for 2 h at 160 °C. The oily product was cooled to 50 °C, dissolved in 20 mL of decalin, and transferred to a suspension of 1 g (25 mmol) of KH in 40 mL of decalin. This mixture was refluxed for 6 h. The supernatant liquid was decanted, and the remaining black tarry residue was washed with pentane to remove excess decalin. It was then dried in vacuo. To separate the K salts of the ligands **15** and **16** from excess KH, the residue was treated with 70 mL of THF and the mixture filtered.

[2,2′-Biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]titanium(IV) Dichloride (17). The THF solution described above was frozen in liquid nitrogen, and 4.8 g (13 mmol) of $TiCl_3(THF)_3$[20] was added in one portion. The reaction mixture was warmed to room temperature and was then refluxed for 3 h. The resulting black solution was oxidized with 50 mL of 6 M HCl in the presence of air and extracted with Et_2O until the organic layer remained colorless. The red solution was dried over $MgSO_4$ and evaporated to a volume of about 70 mL. When it was cooled to 0 °C, **17** crystallized as dark red cubes. The main portion of the product was purified by flash chromatography on silica gel (10/1 pentane/Et_2O): total yield 1.1 g (18% based on 2,2′-diiodobiphenyl). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.02 (s, 6 H), 2.29 (s, 6 H), 4.95 (d, J = 2.81 Hz, 2 H), 6.3 (d, J = 2.81 Hz, 2 H), 7.33–7.49 (m, 8 H). MS (EI): *m/z* 454 (M^+, 26%), 418 (M^+ − HCl, 100%), 382 (M^+ − 2HCl, 10%). Anal. Calcd for $C_{26}H_{24}TiCl_2$: C, 67.95; H, 5.41. Found: C, 68.59; H, 5.31.

[2,2′-Biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]zirconium(IV) Dichloride (18). The THF solution of the potassium salt described above was added in drops to a suspension of 3.65 g (9.7 mmol) of $ZrCl_4(THF)_2$[20] in 40 mL of THF. The mixture was refluxed for 3 h. After the mixture had been cooled to room temperature, the solvent was removed in vacuo. The remaining solid was extracted with hot hexane for 5 days. A pale yellow powder precipitated, and it was filtered and discarded. The hexane extract was evaporated to dryness in vacuo. Recrystallization from 4/1 Et_2O/hexane afforded 210 mg (3% based on 2,2′-diiodobiphenyl) of **18** as yellow plates. ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.0 (s, 6 H), 2.19 (s, 6 H), 4.86 (d, J = 3.05 Hz, 2 H), 6.39 (d, J = 3.05 Hz, 2H), 7.27–7.5 (m, 8 H). MS (EI): *m/z* 498 (M^+, 100%), 460 (M^+ − HCl, 75%). Anal. Calcd for $C_{26}H_{24}ZrCl_2$: C, 62.63; H, 4.85. Found: C, 62.39; H, 4.96.

[6,6′-Dimethyl-2,2′-biphenyldiylbis(3,4-dimethyl-1-cyclopentadienyl)]titanium(IV) Dichloride (22). The same procedure and the same molar ratios used to synthesize **17** were used to synthesize **22** from a solution of 745 mg (1.72 mmol) of 2,2′-diiodo-6,6′-dimethylbiphenyl (**21**)[31] in 15 mL of Et_2O: yield 30 mg (4%) of **22**, a red solid (TLC: R_f 0.24, 10/1 hexanes/Et_2O). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.98 (s, 6 H), 2.07 (s, 6 H), 2.28 (s, 6 H), 4.31 (d, 2 H), 6.31 (d, 2 H), 7.29–7.44 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 15.8, 19.9, 116.1, 120.3, 124.0, 127.0, 128.4, 130.5, 131.0, 131.5, 136.0, 137.8, 142.2. HRMS: calcd for $C_{28}H_{28}TiCl_2$ 482.1051, found 482.1041 (and the observed and calculated patterns of parent peak intensities match).

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Note added in proof: Since this paper was submitted, we have synthesized four analogues of 17 and 18: those in which the methyls of the 3,4-dimethylcyclopentadienyls are replaced by tetramethylenes (yielding "**2-tetrahydroindenyls**") and those in which the biphenyls are replaced by **binaphthyls**. We intend to describe these shortly.

Supplementary Material Available: Listings of NOE and COSY data for 11, X-ray diffraction data for 17, 18, and 22, including tables of crystal data and refinement details, positional parameters, bond distances and angles, and thermal parameters, and a packing diagram for 22 (28 pages). Ordering information is given on any current masthead page.

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1,3-Dipolar Cycloaddition Reactions to the C=X–M Fragment. 7. Reaction of $Ru(CO)_3$(*i*-Pr-DAB) with Dimethyl Acetylenedicarboxylate. X-ray Crystal Structure of the Protonated Initial Bicyclo[2.2.1] Adduct

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In situ prepared $Ru(CO)_3$(*i*-Pr-DAB) reacts instantly at −78 °C with 1 equiv of dimethyl acetylenedicarboxylate. When the reaction mixture is allowed to warm up to room temperature different bicyclic products are obtained, depending on the additional ligand offered. Under 1.1 atm of CO the ruthenabicyclo[2.2.2] complex **9a** can be isolated, which is spectroscopically characterized (IR and ^1H and ^{13}C NMR). This complex does not thermally rearrange to a 1,5-dihydropyrrol-2-one complex **5** as the analogous Fe complexes do, not even at elevated temperatures. When PPh_3 is used instead of CO, the PPh_3-substituted ruthenabicyclo[2.2.2] complex **9b** is formed which has been characterized by an X-ray structure determination. Crystals of **9b**, $C_{35}H_{37}N_2O_7PRu$, are orthorhombic, space group *Pnca*, with cell constants a = 18.699 (1) Å, b = 34.331 (2) Å, c = 11.530 (1) Å, V = 7401.7 Å^3, Z = 8, R = 0.031 (R_w = 0.061) for 5193 reflections with $I > 2.5\sigma(I)$. Addition of HBF_4, at low temperature, immediately after the cycloaddition results in formation of the ruthenabicyclo[2.2.1] complex **10**, $C_{17}H_{23}N_2O_7Ru^+BF_4^-$, of which the structure has been determined by single-crystal X-ray diffraction: crystals of **10** are orthorhombic, space group *Pbca*, a = 13.5335 (8) Å, b = 17.088 (1) Å, c = 20.645 (2) Å, V = 4774.4 (6) Å^3, Z = 8, R = 0.040 (R_w = 0.061) for 3634 reflections with $I > 2.5\sigma(I)$. In complex **10**, the former imine N atom is protonated which prevents the nucleophilic attack of this N-atom on a terminal CO ligand and hence the initial [2.2.1] bicyclic structure is retained. Reaction of $Ru(CO)_3$(*i*-Pr-DAB) with excess DMADC in the absence of an additional ligand results in the formation of (1,4,3a,6a-tetrahydropyrrolo[3,2-*b*]pyrrole)$Ru(CO)_3$ (**11**). The newly formed heterocyclic ligand is readily displaced from the complex at slightly elevated temperature.

Introduction

In earlier papers we have reported the reactions of (1,4-diaza-1,3-butadiene)tricarbonyliron complexes $Fe(CO)_3$(R-DAB)[1] with electron-deficient alkynes following the reaction sequence shown in Scheme I and finally resulting in the formation of (1,5-dihydropyrrol-2-one)tricarbonyliron complexes (**4**).[2-6] The bicyclo[2.2.2] complex (**3**) was the first intermediate that could be isolated and fully characterized. The initial step in which the electron-deficient alkyne reacts with $Fe(CO)_3$(R-DAB) to form the intermediate [2.2.1] bicyclic compound **2** has been described in terms of an oxidative 1,3-dipolar [3 + 2] cycloaddition. This proposal was supported by the fact that is was possible to isolate and characterize a bicyclo[2.2.1] complex (Figure 1)[6] closely resembling the initial cyclo-

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(1) The abbreviations used throughout this text are as follows. The 1,4-diaza 1,3-dienes of formula RN═C(H)C(H)═NR are abbreviated as R-DAB. R-ADA stands for 1,6-di-R-1,6-diazahexa-1,5-diene-3,4-di-R-aminato, RN═C(H)(H)C(NR)(H)C(NR)C(H)═NR, the reductively C–C coupled formally dianionic dimer of R-DAB ligated to two metal atoms. 1,4,3a,6a-Tetrahydropyrrolo[3,2-*b*]pyrrole (Hantzsch-Widman nomenclature) is abbreviated as THPP. AIB stands for 3-amino-4-imino-1-butene, *t*-BuN═C(H)(N-*t*-Bu)C(CF)$_3$═CCF$_3$, the C–C coupling product between *t*-Bu-DAB and hexafluoro-2-butyne, ligated to two metal atoms. AIP stands for 1,2-diamino-2,3-diiminopropane, *t*-BuN═C(H)C(H)(N-*t*-Bu)C(N-*p*-Tol)═N-*p*-Tol, the C–C coupling product between *t*-Bu-DAB and *p*-Tol-carbodiimide, ligated to two metal atoms.

(2) Part I: Frühauf, H.-W.; Seils, F.; Romão, M. J.; Goddard, R. J. *Angew. Chem.* **1983**, *95*, 1014.

(3) Part II: Frühauf, H.-W.; Seils, F.; Goddard, R. J.; Romão, M. J. *Organometallics* **1985**, *4*, 948.

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