served 13.7 (9)° is significantly larger than that observed for other substances containing a three-membered bridge (Table VII) and significantly smaller than that for ferrocenes containing two-membered bridges (Table VII). Recently, the correlations between the iron-to-C_5 crossing distance, ring tilt, and Mössbauer parameters have been established.[47] Several groups[43,44] have theorized that the ring-tilt distortion would

lead to a change in the electronic structure of the ferrocene. Ferrocene oxidation should lead to the loss of a weakly bonding e_{2g} ($3d_{xy}$, $3d_{x^2y^2}$) electron; however, the only previous report[48] of changes in the ferrocene conformation upon oxidation is a change is symmetry from D_{5d} to D_{5h}. Ballhausen and Dahl[43] also point out that ring-tilt distortions of up to 45° are not reflected in metal–ring bond energy changes. Consequently, the observed 13.7 (9)° ring tilt may result from the minimization of crystal packing forces.

In view of this large ring tilt, another structural anomoly of the [Fc(CH$_2$)$_3^+$·] radical ion should be discussed. The average carbon–carbon bond length in C_5 rings of ferrocenium ions is 1.42 Å.[4,5,9,45] In [Fe(CH$_2$)$_3^+$·], however, four of the carbon–carbon bond distances average 1.411 Å, while the C2–C3 distance is significantly shorter, 1.374 (4) Å, between atoms that are the farthest from the Fe atom (i.e., Fe–C2 is 2.102 (3) Å and Fe–C3 is 2.096 (3) Å). For the ferrocene compounds α-oxo-1,1'-trimethyleneferrocene and α-keto-α'-phenyl-1,1'-trimethyleneferrocene, which have smaller C_5 inclinations (Table VII) and which are not oxidized, similar bond shortening is not observed. With removal of a $3d_{xy}$, $3d_{x^2-y^2}$ electron of the Fe from the e_{2g} weakly bonding orbital and a decrease in the interaction distance between the Fe and C2 and C3, the possibility increases of localizing the electrons on C2 and C3, therefore enhancing the C2–C3 double-bond character.

Registry No. [Fc(CH$_2$)$_3^+$·][(TCNQ)$_2^-$·], 75600-07-6; Fc(CH$_2$)$_3$, 12302-04-4; TCNQ, 1518-16-7.

Supplementary Material Available: A listing of F_o and F_c (8 pages). Ordering information is given on any current masthead page.

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Cumulene-Derived Metallocyclic Complexes. 2. Syntheses and Characterization of 2,5-Diethylidene- and 2,4-Dimethylenemetallocyclopentanes

J. RUSSELL SCHMIDT and D. MICHAEL DUGGAN*

Two new exo unsaturated metallocyclopentanes have been obtained in high yield by the reaction of allene and 1,3-dimethylallene with [(C$_5$Me$_5$)$_2$ZrN$_2$]$_2$N$_2$. The allene-derived complex, I, has been structurally characterized by using single-crystal X-ray crystallography and both ^{1}H and ^{13}C NMR spectroscopy of solutions. The *exo*-methylene groups are found in the 2 and 4 positions on the metallocyclic ring. Rapid ring inversion averages axial and equational environments on the ^{1}H NMR time scale at room temperature in toluene solution. A ^{13}C NMR absorption at ~205 ppm downfield from Me$_4$Si is a characteristic of an sp^2 carbon bound to the zirconium atom. The structure of the product derived from 1,3-dimethylallene was defined from the consideration of ^{1}H and ^{13}C NMR data in comparison to I. The ethylidene groups are found to substitute the metallocyclopentane ring in the symmetrically disposed 2 and 5 positions, with the methyl substitutents in the *E,E* configuration (relative to the metal). This product (including its enantiomer) is the only compound found to have been formed out of 48 possible geometric isomers, region isomers, and stereoisomers. In that the 1,3-dimethylallene used was a racemic mixture, the identity of the metallocyclic product demonstrates greater than 95% chiral selectivity in that only *R,R* and *S,S* pairs are oxidatively coupled in the carbon–carbon bond-forming process.

Introduction

We have been studying the organometallic chemistry of cumulenes for three reasons: (1) There is much inherent interest in the use of CO_2 as a natural resource; (2) Heterocumulenes such as ketenes, carbodiimides, and ketenimines have displayed considerable use in organic synthesis, yet their utilization in the presence of metal complexes has not been thoroughly explored: (3) The formation and characterization of metallocyclic complexes has attacted much attention in

recent years, and we often find metal–cumulene reactions to give rise to metallocyclic products.

In this paper, we shall discuss the preparation and physical properties of two new metallocyclic complexes—these being derived from allene and 1,3-dimethylallene. These complexes complete the list of observed structural types for the coupling of common unsaturated organic molecules into 5-membered metallocycles. For enumeration, saturated metallocyclopentanes can be formed from a carbon–carbon coupling process
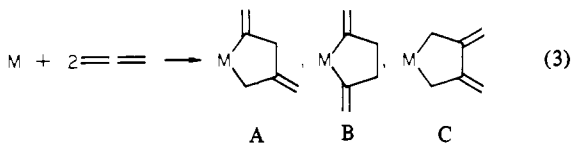
involving olefins (eq 1).[1] Internally unsaturated metallo-

$$M + \| \longrightarrow M\langle\rangle \qquad (1)$$
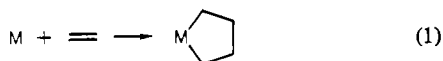
cyclopentadienes can be obtained by acetylene coupling (eq 2).[2] Externally unsaturated metallocyclopentanes have been
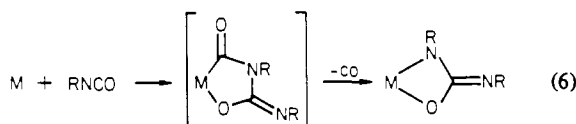
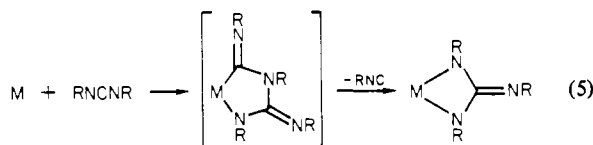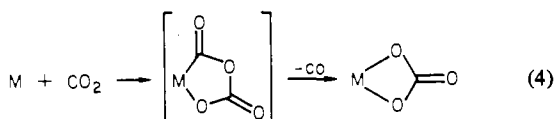$$M + 2\|\!\|\!\| \longrightarrow M\langle\rangle \qquad (2)$$
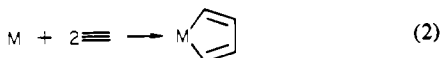
isolated from reactions of allenes (eq 3). This paper reports

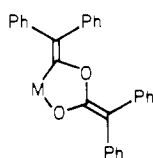$$M + 2\!=\!\!=\!\!= \longrightarrow \qquad (3)$$

A B C

examples of types A and B, where the only previously known bis(allene) metallocycle is of type C.[3]

The identification of type A is of particular interest, in that the asymmetric metallocycle has also been suggested as playing a major role in the organometallic reactions of CO_2,[4,5] carbodiimides,[6] ketenes,[7] and isocyanates.[5] The stability of the bis(heterocumulene) metallocycles has often been found to be low—for in these cases the loss of a molecule of CO or RNC may produce the following transformations in eq 4–6. Each

$$M + CO_2 \longrightarrow \left[\right] \xrightarrow{-CO} \qquad (4)$$

$$M + RNCNR \longrightarrow \left[\right] \xrightarrow{-RNC} \qquad (5)$$

$$M + RNCO \longrightarrow \left[\right] \xrightarrow{-CO} \qquad (6)$$

of these general types of metal-induced elimination reactions has been observed (although the products have not necessarily been mononuclear, as drawn). While an asymmetric metallocyclic complex involving any of these three reactants has been isolated in only one instance,[4a] its existence as a key intermediate has been suggested[4-6] in each case.

The asymmetric bis(diphenylketene) metallocycle

Table I. Positional Parameters for Nonhydrogen Atoms of $Zr(C_5Me_5)_2(C_3H_4)_2$[a]

	x	y	z
Zr	0.77326 (5)	0.31649 (5)	0.54871 (8)
C(11)[b]	0.8405 (6)	0.4689 (6)	0.6318 (9)
C(12)	0.7496 (0)	0.4723 (6)	0.6366 (10)
C(13)	0.7338 (7)	0.4102 (7)	0.7399 (11)
C(14)	0.8166 (7)	0.3694 (7)	0.7459 (9)
C(15)	0.8798 (6)	0.4062 (7)	0.7309 (9)
C(21)	0.8867 (7)	0.5336 (6)	0.5542 (11)
C(22)	0.6888 (7)	0.5406 (8)	0.5628 (13)
C(23)	0.6499 (8)	0.4058 (9)	0.8021 (13)
C(24)	0.8299 (9)	0.3040 (8)	0.9120 (10)
C(25)	0.9761 (6)	0.3939 (8)	0.7709 (12)
C(31)	0.6511 (6)	0.3106 (8)	0.3436 (11)
C(32)	0.6100 (6)	0.3070 (7)	0.4601 (12)
C(33)	0.6337 (6)	0.2252 (7)	0.5301 (10)
C(34)	0.6871 (5)	0.1781 (7)	0.4524 (10)
C(35)	0.6978 (8)	0.2306 (10)	0.3397 (5)
C(41)	0.6354 (9)	0.3804 (9)	0.2340 (14)
C(42)	0.5352 (7)	0.3701 (9)	0.4839 (10)
C(43)	0.6000 (7)	0.1877 (9)	0.6481 (11)
C(44)	0.7118 (8)	0.0816 (7)	0.4754 (13)
C(45)	0.7374 (9)	0.1993 (9)	0.2209 (11)
C(6)	0.8660 (7)	0.3922 (8)	0.2959 (10)
C(5)	0.8697 (6)	0.3387 (6)	0.4029 (9)
C(4)	0.2717 (7)	0.4420 (11)	0.0041 (6)
C(1)	0.9317 (7)	0.1081 (8)	0.4507 (12)
C(2)	0.9170 (6)	0.1884 (7)	0.5019 (10)
C(3)	0.8732 (6)	0.2030 (6)	0.6223 (10)

[a] Estimated standard deviation of the least significant figure is shown in parentheses. [b] C(11)–C(15) and C(21)–C(25) label the inner and outer carbons on one C_5Me_5 ring, respectively; C(31)–C(35) and C(41)–C(45) similarly label the other ring.

would not be conducive to neutral molecule elimination; accordingly this type of product has been found to be stable.[7]

Allene reactions with metal complexes would also be expected to yield stable metallocyclic products—but it is generally found that higher oligomerization occurs for the coordinately unsaturated group 8 complexes with which they have been studied. Prior to this report no metal system has been described in the literature which has effected discrete oxidative coupling of both allene and substituted allenes.
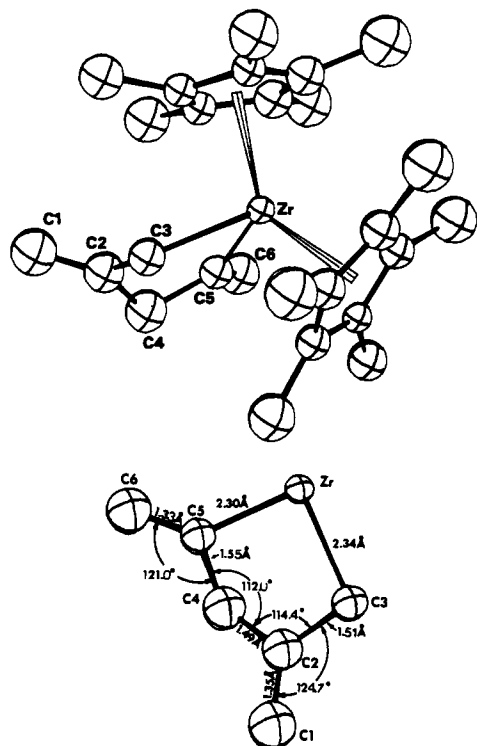
The ability to prepare stable allene-derived metallocycles immediately suggests the exploration of the mechanism of coupling, the possibility of cocoupling with heterocumulenes, and the investigation of further reactivity of exo unsaturated metallocycles with unsaturated organics such as acetylenes. These topics will be covered in future reports.

Experimental Section

The reaction of $[(C_5Me_5)_2ZrN_2]_2N_2$[8] with allene in toluene results in the absorption of 2 mol of allene/mol of zirconocene and release of all dinitrogen. This has been measured on a vacuum-line system by using traps at $-78\ °C$ to separate the allene from the toluene and traps at $-196\ °C$ to separate the N_2 from the allene. When the remaining solution is evaporated, orange crystalline material (I) is obtained. It has been found to be $\sim$95% pure and is thoroughly characterized in the following paragraphs.

The complex, I, crystallizes in the $P2_1/c$ group with unit cell parameters $a = 15.601$ (3) Å, $b = 15.026$ (2) Å, $c = 10.034$ (1) Å, and $\beta = 100.28$ (1)°. It was found that the crystal decomposed under X-ray exposure, so 2002 unique and nonsystematically absent data (1600 > 3σ) were collected in two spheres (0–30° and 30–40° in 2θ) at scan rates of 4–29°/min on a Syntex $P2_1$ diffractometer with graphite-crystal-monochromated Mo Kα radiation. Three standards were measured and found to fall off linearly and isotropically with time to 60% of their initial value during the total 40 h of X-ray exposure. All data were corrected for decomposition. The structure was solved by using MULTAN[9] and refined to convergence by using

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Figure 1. ORTEP drawings of $Zr(C_5Me_5)_2(C_3H_4)_2$, showing two views of the metallocyclopentane moiety. Bond distances and angles indicated are from the final cycle of anisotropic refinement.

full-matrix least squares[10] with isotropic thermal parameters to a conventional R factor of 0.077 (1600 reflections) not including hydrogens. A difference Fourier run at this point revealed no significant areas of electron density (positive or negative), verifying the general correctness of the model.

Anisotropic refinement was carried out through four complete cycles, refining the rings and the metallocycle separately due to the program size limitation. After three complete cycles the unweighted R factor had converged to 0.071 (all data) not including hydrogens. Due to the large number of free-rotating hydrogens (30) and the limitation of data quality imposed by the deterioration of the crystal (although apparently well corrected) no further elaboration of the model was attempted. No change in parameter during the last cycle was more than 60% of its standard deviation. A difference Fourier at this point revealed no peaks larger than 1 e/$Å^3$. A table of fractional coordinates appears as Table I. Bond distances and angles with standard deviations and a complete listing of F_o and F_c are available as supplementary material.

The molecular structure of $Zr(C_5Me_5)_2(C_3H_4)_2$ is shown in Figure 1. Both "allene" moieties are bent $\sim 60°$ from linearity, and the *exo*-methylene carbons C_6 and C_1 are at normal C–C double-bond distances from the atoms to which they are bound. A comparison to the symmetric type C structures, reported earlier,[3] is warranted. For $(acac)Ir(C_3H_4)_2(py)$ and $(acac)Rh(C_3H_4)_2(py)_2$ the intraring C–C distances are all ~ 1.50 Å and the *exo*-methylene C–C distances are 1.34–1.42 Å, similar to our findings. But for the symmetric systems the metallocycle is twisted about the central C–C bond such that the allene moieties form a dihedral angle (for the iridium case) of 38°. The iridium lies out of the plane of either of the allene moieties. For $Zr(C_5Me_5)_2(C_3H_4)_2$ the Zr atom lies approximately in the plane of the C_4, C_5, C_6 moiety and 1.65 Å out of the plane of the (terminally bound) C_1, C_2, C_3 moiety. In that the atoms Zr, C_3, C_4, C_5, and C_6 are approximately coplanar, the puckering of the metallocyclic ring is due to the C_2, C_1 fragment—these atoms lying out of the ring plane by 0.577 and 1.56 Å, respectively.

(9) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declerq, P. D. "MULTAN 77"; Department of Physics, University of York, York, England; Laboratoire de Chemie Physique et Cristallographique, Batiment Lavoisier, University of Louvain, Louvain, Belgium.

(10) Scattering factors from: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

The NMR and infrared data obtained for I are as follows. ^1H NMR spectrum (ppm downfield from Me$_4$Si) (numerical labeling consistent with Figure 1): 1.80 (ring methyl), 5.69 (d of t, $J = 3.5$ Hz, $J_{allylic} = 1.8$ Hz, C(5)=CH$_2$), 4.04 (d of t, $J = 3.5$ Hz, $J_{allylic} = 2.4$ Hz, C(5)=CH$_2$), 4.45 and 4.48 (second order, C(2)=CH$_2$), 3.05 (br, C(4)H$_2$), 1.35 (t, $J_{allylic} = 1.2$ Hz, C(3)H$_2$). ^{13}C NMR spectrum (shifts downfield from Me$_4$Si): 11.62 (ring methyls), 119.4 (ring inner carbons), 209.0 (C(5)), 153.3 (C(2)), 55.2 and 57.0 (C(3) and C(4)), 114.3 (C(5)=CH$_2$), 101.3 (C(2)=CH$_2$). Infrared spectrum (allene-related peaks only): 1605 (mw, C=C stretch), 840 and 880 cm^{-1} (ms, δ(C–H$_2$)). It should be noted that the infrared absorptions for the permethylzirconocene moiety are sufficiently few and weak to permit ready identification of absorptions due to coordinated allene.

Reaction of $[(C_5Me_5)_2ZrN_2]_2N_2$ with 1,3-dimethylallene may be carried out most readily in toluene, but the experiment described here used mesitylene in order to facilitate quantitative separation of the unreacted cumulene. A 300-mg (0.372 mmol) sample of the dinitrogen complex was placed with 10 mL of mesitylene (distilled in from a flask containing "titanocene hydride" drying agent), and then 1.610 mmol of 1,3-dimethylallene was condensed in at -196 °C. The vessel was closed and allowed to warm to room temperature. The reaction occurred rapidly at $\sim-10°$ as evidenced by the loss of violet color and formation of a yellow solution. The remaining solution was cooled to -35 °C, and the excess cumulene was then removed from the reaction vessel (along with the released N$_2$) by using a Toepler pump system with 0, -40, -78, and -196 °C traps intervening. Recovered N$_2$ indicated that all N$_2$ had been released, and recovered cumulene indicated that 2.0 molecules of 1,3-dimethylallene had reacted per mole of zirconium. The mesitylene was completely evaporated from the reaction vessel, and the yellow crystalline product was dissolved in butane at -78 °C. Filtration revealed no residual solid, and slow evaporation of the butane yielded the product, II, for which the spectroscopic data are reported. Although crystalline material was obtained, the crystals were found to be too soft to handle, defeating attempts at X-ray study.
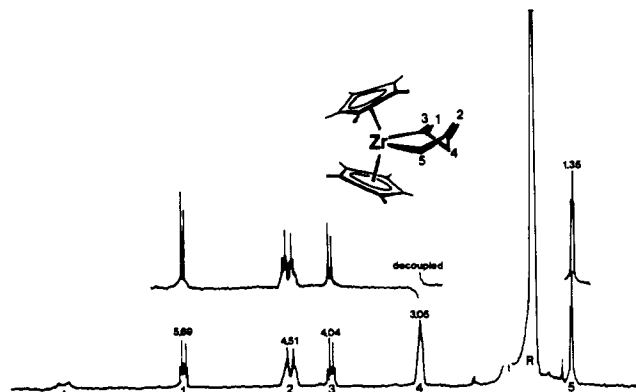
The yellow solid was studied by using infrared and both ^1H and ^{13}C NMR spectroscopy. There is no doubt from the ^1H NMR that the material consists of permethylzirconocene units with two bonded 1,3-dimethylallenes and the product is at least 95% free of any other compounds. Chemical analyses for these permethylzirconocene systems have been found to be often of low accuracy and to be irreproducible, so we cannot report valid elemental data. A much more sensitive determination of composition can be obtained from the vacuum-line measurements and NMR. The most critical points to check in the ^1H NMR studies are for the presence of unassignable peaks and the integrations. The spectrum reproduced in Figure 4 shows no significant peaks other than those assignable to the suggested structure. Integration of the methyl absorptions of 1,3-dimethylallene relative to the ring-methyl absorptions provides a convenient method for the determination of the number of cumulene molecules per zirconocene unit. Since the downfield allene methyls, peak 3, fall on the edge of the ring-methyl absorption, the relative areas of the upfield allene methyls, peak 4, and the sum of the ring and downfield absorptions were measured. If a 1:1 complex were to have been formed, this area ratio would be expected to be 3:33 or 1:11, whereas a 2:1 allene to zirconium complex would show a 6:36 or 1:6 ratio. The ratio was found to be 1:6 ± 0.5, and this clearly identifies the complex as a 2:1 1,3-dimethylallene adduct, consistent with the vacuum-line measurements.

The NMR and infrared data obtained on this complex are summarized below, and comments on unusual features or implications are deferred to the Results and Discussion. ^1H NMR spectrum (shifts downfield from Me$_4$Si in ppm): 1.81 (ring methyl), 3.72 (q of d, $J_q = 6.5$ Hz, $J_d = 2.6$ Hz, =CH–CH$_3$), 2.61 (br, q, CHCH$_3$), 1.71, (d of d, $J_1 = 6.5$ Hz, $J_{homoallylic} = 1.2$ Hz, =CHCH$_3$), 1.26, (d, $J = 7.0$ Hz, CHCH$_3$. ^{13}C NMR data (ppm downfield from Me$_4$Si): 12.33 (ring methyls), 119.8 (ring inner carbons), 205.14 (C(2)), 49.68 (C(3)), 120.54 (=CHCH$_3$), 22.3 and 17.32 (=CHCH$_3$ and CHCH$_3$). The allene-related infrared absorptions are at 1575 (C=C stretch, mw) and 800 cm^{-1} (δ(CH$_2$), mw, br).

Results and Discussion

We have isolated in nearly quantitative yield two new complexes of permethylzirconcene; one contains 2 mol of allene/mol of zirconium, and the other has incorporated 1,3-dimethylallene in the same molar ratio (see Experimental

Figure 2. Proton NMR spectrum of $Zn(C_5Me_5)_2(C_3H_4)_2$ in toluene-d_8 solution taken with a Bruker WH-90 instrument. The upfield tol-d_7 impurity band has been removed for clarity and marked with a t. The peaks are labeled in descending δ and correspond to the assignments indicated on the inset drawing. The absorption due to the C_5Me_5 rings is labeled R.

Section). The bis(allene) complex has been structurally identified by X-ray methods (Figure 1), and its solution structure will be shown by NMR evidence to be similar. The complex of 1,3-dimethylallene could not be characterized by X-ray crystallography due to the inability to obtain suitable crystals. However, arguments will be presented below, based on spectroscopic data which limit the number of possible structures. One purpose of this report is to present a discussion of spectroscopic data for these exo unsaturated metallocyclopentanes which may subsequently serve as a basis for the structural elucidation of related compounds.

There are four distinct forms of isomerism that may exist for bis(cumulene) complexes. The first form is quite uncommon but should be considered as a formality, i.e., where the complex formed has two independently coordinated cumulene moieties. One may of course envisage situations where geometric variations on such complexes exist, although some may well be equilibrated by rapid thermal motion. The three other types of isomerism all relate to the formation of exo unsaturated metallocyclopentanes, the most fundamental distinction being the pattern of unsaturation. As illustrated in the Introduction, exo unsaturated species of types A–C may exist. When dealing with substituted allenes, we also have the possibility of regioisomers and stereoisomers.

For an (unsubstituted) allene-derived metallocyclic complex there are three possible structural isomers. We may easily distinguish between these by using proton and carbon NMR. For a 1,3-dimethylallene-derived metallocyclic complex there are 48 possible isomers! Many of these may be uniquely identified by using spectroscopic evidence and chemical reason. The two reactions reported here each produce only *one* (>90%) cumulene-derived product. We shall comment on the most appropriate interpretation of this selectivity after discussion of the characterization of the complexes.

First let us identify the important spectral features of the asymmetric allene-derived metallocycle $(C_5Me_5)_2Zr(C_3H_4)_2$, I. The proton NMR spectrum is shown as Figure 2. Aside from the single peak associated with the C_5Me_5 methyl groups there are peaks due to four vinylidene and four methylene protons. The most interesting features of the spectrum are associated with the vinylidene and methylene groups α to the metal. In both cases the metal has a large effect on the proton chemical shift. The α-methylene, labeled peak 5 in Figure 2, absorbs at δ 1.35 which is considerably upfield of the typical allylic methylene (generally falling in the 1.8–2.3-ppm range). The two α-vinylidene protons fall at 5.69 and 4.04 ppm. Each is split by the other and by the doubly allylic methylene proton (labeled 4 in Figure 2). The fact that the doubly allylic hy-

drogens are *equivalent* both in chemical shift and in coupling interactions demonstrates that a rapid metallocycle inversion motion is taking place in solution.

The geminal coupling for the α-vinylidene group is 3.5 Hz while the allylic couplings for the 5.69- and 4.04-ppm resonances are 1.8 and 2.4 Hz, respectively. The question arises as to the correspondence between these peaks (labeled 1 and 3 in Figure 2) and the *endo*- and *exo*-hydrogens on C6. Both coupling constant and chemical shift arguments may be used to answer this question. Allylic coupling constants cover a range of values from $+1$ to -3 Hz, depending upon the dihedral angle between the plane of the double bond and the C–C–H-(allylic) plane. The relative magnitude of cis and trans couplings also depends upon the dihedral angle. For most acyclic molecules the cis allylic coupling is slightly larger than the trans.[11] However, for cyclic systems the trans coupling is often larger. It has been generalized that the absolute value of trans allylic coupling is larger for molecules with dihedral angles larger than 45°.[12] With the rapid ring inversion in mind, an average dihedral angle of 65° may be calculated for the bis-(allene) complex. This was estimated by using a scale model derived from the actual X-ray solution of the crystalline structure. It is then expected that the trans allylic coupling would be larger for our complex. This suggests that the *endo*-hydrogen absorbs at 4.04 ppm and the exo at 5.69 ppm.

The assignment made above is supported by ^{1}H NMR observations on the most structurally related organometallic compounds presently in the literature, e.g., allene adducts of the general structure
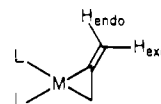
For the nickel, palladium, and platinum series where L = PPh_3, it was found that the *exo*-proton is always downfield of the *endo*-proton, generally by $\sim$1.4 ppm.[13] This is consistent with our assignment based on coupling constant logic, vide supra. This assignment will be of use later when the effects of substitution on the ^{1}H NMR spectrum will be used to deduce stereochemical patterns of substitution.

Another particularly characteristic feature of the ^{1}H NMR spectrum of $(C_5Me_5)_2Zr(C_3H_4)_2$, I, is the resonance at 3.05 ppm. The complexity of this broad peak, plus the decoupling experiments, proves that it corresponds to the doubly allylic hydrogens. Since the asymmetric form of an allene-derived metallocycle is the only form possessing doubly allylic hydrogens, it is only for this particular isomer that a broad peak in a vicinity of 3 ppm should be observed.

The ^{13}C NMR observations for I also prove to be characteristic of the asymmetric structure. The bottom half of Figure 3 shows the spectrum, where the expected six peaks due to metallocyclic carbons are labeled to correspond to the inset drawing. There are three regions of importance: 50–60, 100–120, and 150–210 ppm. These correspond to sp^3 carbons, vinylidene sp^2 carbons, and quaternary sp^2 carbons, respectively. The sp^3 carbons appear at quite similar shifts, whether bound directly to the metal or not. For the sp^2 carbons this is not the case. The C(1)–C(2) double bond has ^{13}C resonances nearly identical with those found for methylenecyclopentane or for 1,3-dimethylenecyclopentane (peaks are found at 104.9 and 153.1 ppm for terminal and quaternary sp^2 carbons, respectively, in the former case).[14] However the α-vinylidene carbons for $(C_5Me_5)_2Zr(C_3H_4)_2$ are assigned at

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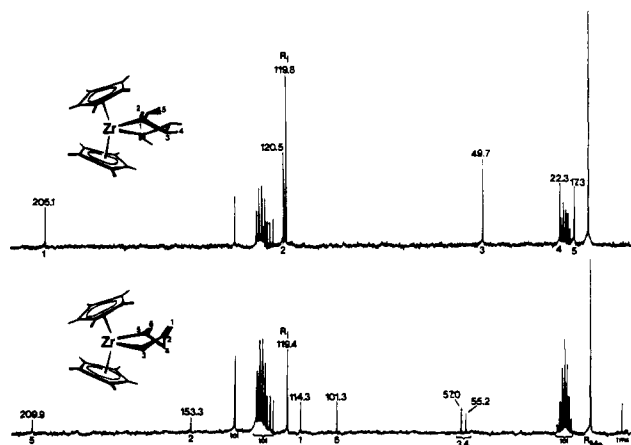
Figure 3. ^{13}C NMR spectra of $Zr(C_5Me_5)_2(C_3H_4)_2$ (bottom) and $Zr(C_5Me_5)_2(C_5H_8)_2$ (top) in toluene-d_8, taken with a Bruker WH-90 instrument. The absorptions due to the solvent are indicated on the bottom spectrum. The C_5Me_5 methyl absorptions are labeled R_{Me} while the inner carbons are labeled R_i. All assignments are indicated in the inset drawings. For the bottom spectrum no definite assignment can be made for carbons 3 and 4.

114.3 and 209.9 ppm for terminal and quaternary, respectively. This represents a major perturbation of the double bond due to the metal coordination. The most characteristic peak in the ^{13}C spectrum is that due to the metal-bound sp^2 carbon, falling at 209.9 ppm. As further examples will document, the appearance of a peak in the 200-ppm region may be taken as clear evidence for the α-vinylidene structure.

Now let us turn to the structural identification of II, $(C_5Me_5)_2Zr(C_5H_8)_2$. We will first look at the NMR spectra in order to identify which of the 48 possible isomers of a metallocyclic complexex this might be. Then we will address the question as to whether this may in fact be an independently coordinated bis(1,3-dimethylallene) system.

The ^1H NMR spectrum of the 1,3-dimethylallene-derived product, $(C_5Me_5)_2Zr(C_5H_8)_2$, is shown as Figure 4. It is clear at a glance that there are only four non-C_5Me_5 absorptions. The methyl groups are readily identified as accounting for peaks 3 and 4, whereas single protons adjacent to methyl groups produce the quartets at peaks 1 and 2. We may compare the chemical shift *and* allylic coupling constant of the furthest downfield peak (peak 1) of II with the data obtained for the endo vinylidene hydrogen of I. The respective values are 3.72 vs. 4.04 ppm and 2.6 v. 2.4 Hz. This is strong support for the existence in the structure of the fragment
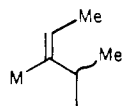
The absence of a ^1H NMR resonance at 3 ppm and the presence of the 205-ppm absorbance in the ^{13}C spectrum (top of Figure 3) identify the fundamental structure as type B. The simplicity of both the proton and carbon spectra imply high substitutional symmetry. Spectroscopic analysis thereby limits the possible structures for II to two choices
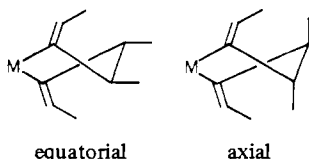

each one classified according to the orientation of the equivalent methyl groups on carbons β to the metal. We have made models of these structures on the basis of the inter-ring angle
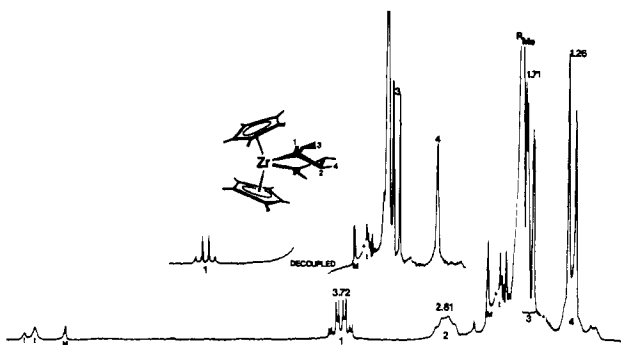
Figure 4. ^1H NMR spectrum of $Zr(C_5Me_5)_2(C_5H_8)_2$ in toluene-d_8, taken with a Bruker WH-90 instrument. Side bands have been removed for clarity and the spaces marked with a dot. A small amount of mesitylene impurity is present (the reaction solvent), and the absorptions from it are marked with an M. The toluene-d_7 impurity signals are maked t. Chemical shifts are in ppm downfield from Me_4Si and the C_5Me_5 ring absorption is labeled R_{Me}. The peak assignments are as indicated on the inset drawing.

and distances found for I. Three points are obvious from these models: (1) The axial isomer requires steric interaction between the β-methyl groups and the ring-methyl groups (C–C distances during ring rotations ranging from 1.5 to 2.5 A); (2) The equatorial isomer has some steric strain imposed by the proximity of the exo and equatorial methyl groups; (3) The dihedral angles for the β-hydrogens relative to the double bonds are $\sim$30 and $\sim$80° for the axial and equatorial forms, respectively. This latter information suggests that only for the equatorial case should allylic and homoallylic coupling constants be substantial in magnitude. The observed constants are $|J_{12}| = 2.6$ Hz for the allylic coupling (transoid) and $|J_{32}| = 1.2$ Hz for the (cisoid) homoallylic coupling. The allylic coupling is larger than that found for I ($|J_{34}| = 2.4$ Hz), consistent with a large dihedral angle. The homoallylic coupling is larger than one would expect for a cisoid interaction where the dihedral angle is small and a freely rotating methyl group is involved. The structure we favor is therefore the equatorial form, shown in Figures 3 and 4. It should be remarked that the axial and equatorial forms can be interconverted by ring inversion, but due to the close axial methyl interaction with the rings this isomer should be a higher energy form, the equatorial being favored as seems to be the case.

A word should be said regarding the relationship between the structure of II most consistent with the spectroscopic data and the predictions that one would make from models. The bent permethylzirconocene moiety has a very well-defined wedgelike region of access to the metal. The angle between the ring normals is $\sim$145° and cannot be smaller due to methyl repulsions on the back side (away from the wedge). Given the high symmetry and low flexibility of the metallocene wedge, one can easily convince oneself as to the relatively undesirable nature of three basic substitutional patterns that may arise from allene reactions:
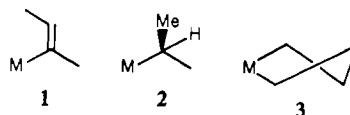
The avoidance of pattern **2** eliminates metallocycles of types A and C from the list of possibilities. The fact that endo substitution (pattern **1**) and axial sp^3 substituion is not observed for this reaction does not indicate whether these forms are actually sterically forbidden or whether they are *kinetically* avoided. This point will be addressed in a later paper.

The possibility of 1,3-dimethylallene forming a complex with two independently coordinated allenes is remote at best. The only conceivable structure of this type that would be consistent

with the spectroscopic data is
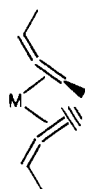
The major problem lies in the steric interaction of the α-methyl groups with the rings. This Zr(II) structure pulls the methyl groups much further into the wedge than required for the metallocyclic possibility. Also, we have been unable to displace allenes from these molecules by further reaction with allenes,

acetylene, or CO_2. This seems as well to suggest the likelyhood of a very stable Zr(IV) metallocyclic structure.

In a later paper we will show that the bis(allene) adduct is in fact an intermediate in the thermal rearrangment of II.

Registry No. I, 75125-14-3; II, 75112-05-9; $[(C_5Me_5)_2ZrN_2]_2N_2$, 54387-50-7; allene, 463-49-0; 1,3-dimethylallene, 28383-16-6.

Supplementary Material Available: A listing of structure factor amplitudes and thermal parameters and pertinent intramolecular distances and angles (17 pages). Ordering information is given on any current masthead page.

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Oxidative Addition of Acyl Chlorides to Chlorotris(dimethylphenylphosphine) Complexes of Rhodium(I) and Iridium(I). Crystal and Molecular Structure of [RhCl(COCH₃)(PMe₂Ph)₃]PF₆, an Acetyl Complex Which Undergoes Unusually Fast Methyl Migration in Solution

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Acyl chlorides RCOCl react with $MClL_3$ (M = Rh, Ir; L = PMe_2Ph) to give six-coordinate acyl–rhodium(III) or –iridium(III) complexes $MCl_2(COR)L_3$ (M = Ir, R = CH_3 (1), $CH_2CH_2CH_3$ (2), $CH(CH_3)_2$ (3); M = Rh, R = CH_3 (4), CH_2CH_3 (5), $CH(CH_3)_2$ (6)). Treatment of 1 and 2 with NH_4PF_6 generates six-coordinate alkylcarbonyl salts $[IrClR(CO)L_3]PF_6$ (R = CH_3 (7), $CH_2CH_2CH_3$ (8)) as a result of alkyl group migration, whereas 3 fails to react. Similar treatment of the rhodium complex 4 in the absence of oxygen gives $[RhCl(COCH_3)L_3]PF_6$ (9), which is shown by three-dimensional X-ray structural analysis to contain an approximately square-pyramidal cation with an apical acetyl group. Crystals of 9 are monoclinic, of space group $P2_1/c$, with $a = 12.685$ (2) Å, $b = 15.209$ (3) Å, $c = 16.552$ (2) Å, $\beta = 95.96$ (1)°, and $Z = 4$. The structure was solved by conventional Patterson and difference Fourier syntheses and refined by full-matrix least-squares methods to a conventional R factor of 0.044 (4949 reflections). Important bond lengths are Rh–C(acyl) = 1.971 (5) Å, Rh–Cl = 2.391 (1) Å, Rh–P(trans to Cl) = 2.285 (1) Å, Rh–P(trans to L) = 2.389 (4) Å, and C(acyl)–O = 1.184 (6) Å. A nonbonded interaction between the acetyl methyl group and the chlorine ligand shifts the latter from an ideal equatorial site toward the vacant apical position. In solution, 9 is in equilibrium with a six-coordinate methylcarbonylrhodium(III) complex $[RhCl(CH_3)(CO)L_3]PF_6$ (10) analogous to 7. Methyl migration occurs at an intermediate rate on the ^1H and ^{31}P NMR time scales at room temperature but is slow at –70 °C, where the ratio of 9 to 10 is ca. 2:1. Possible reasons for this behavior are (1) the structure of 9 in the solid state may be close to that of the transition state for methyl migration and (2) the positive charge on the metal atom may help to destabilize the ground states of 9 and 10 relative to the transition state by reducing π bonding to the acyl and CO groups, respectively.

Introduction

Acyl chlorides RCOCl oxidatively add to the planar d^8 complexes $MCl(CO)L_2$ (M = Rh, Ir; L = various tertiary phosphines and arsines) to give six-coordinate acyl–metal(III) complexes $MCl_2(COR)(CO)L_2$.[1–4] The corresponding additions to $IrCl(N_2)(PPh_3)_2$[4] or to $MClL_3$ (L = PPh_3, M = Rh, Ir; L = $PMePh_2$, M = Ir)[4–11] give initially five-coordinate

Scheme I
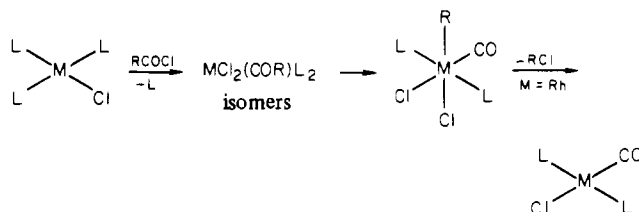
acyl–metal(III) complexes $MCl_2(COR)L_2$ which subsequently isomerize by alkyl group migration to form six-coordinate alkyl–metal(III) complexes $MCl_2R(CO)L_2$ (Scheme I). In the case of rhodium, ready elimination of RCl (or olefin and HCl) gives $RhCl(CO)L_2$ as the final product. An interesting

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