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Synthesis and Structure of a Chelated Manganese Carbene–Alkene Complex

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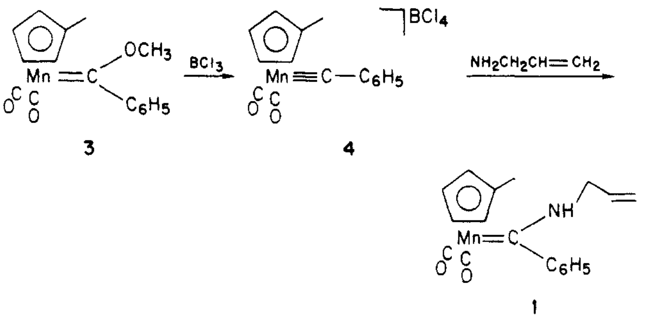
Reaction of $(\eta^5\text{-}C_5H_4(CH_3))Mn(CO)_2(\equiv CC_6H_5)][BCl_4]$ with excess allylamine generated $(\eta^5\text{-}C_5H_4(CH_3))Mn(CO)_2[C(C_6H_5)(NHCH_2CH{=}CH_2)]$, **1**, as a 2.8:1.0 mixture of isomers. Isomers of **1** exist as a consequence of restricted carbene carbon–nitrogen bond rotation. High-temperature NMR studies on $(\eta^5\text{-}C_5H_4(CH_3))Mn(CO)_2[C(C_6H_5)(N(CH_3)_2)]$ establish a minimum barrier to rotation around the C–N bond of 21 kcal/mol for this complex. Low-temperature photolysis of **1** resulted in the formation of $(\eta^5\text{-}C_5H_4(CH_3))Mn(CO)[C(C_6H_5)(\eta^2\text{-}NHCH_2CH{=}CH_2)]$, **2**. Infrared and ^1H and ^{13}C NMR data are reported for both **1** and **2**. The X-ray crystal structure of **2** shows a roughly octahedral arrangement of the ligands in which the carbene is cis and approximately parallel to the olefin. The compound crystallizes in the space group $P2_1/c$ with four molecules per unit cell (a = 7.936 (2) Å, b = 14.593 (5) Å, c = 12.569 (5) Å, β = 99.08 (3)°, V = 1437.4 Å^3, ρ(calcd) = 1.420 g/cm^3). Full-matrix least-squares refinement of 121 parameters using 866 data with $I \geq 2\sigma(I)$ converged with R = 0.074 and R_2 = 0.052. The geometry of this first-row transition-metal carbene–alkene complex is compared to the geometry reported by Casey and co-workers for the analogous chelating carbene–alkene linkage in a tungsten derivative, $(CO)_4W[C(tolyl)(\eta^2\text{-}NHCH_2CH{=}CH_2)]$.

Metal carbene–alkene complexes have been postulated as key intermediates in olefin metathesis[1] as well as in transition-metal-mediated cyclopropanation reactions.[2] In both of these reaction types, the carbene–alkene species is thought to decompose via a metallocyclobutane intermediate or a metallocyclobutane-like transition state. Presently there is limited experimental evidence to support these assertions, and only a few examples of stable carbene–alkene complexes have been reported.[3-12] In most cases the complexes are stabilized by chelation of the olefin and/or by heteroatom substituents on the carbene, although Schrock[9] and Grevels[10] have prepared carbene–alkene compounds which enjoy neither of these modes of stabilization. Casey has reported a series of (η^2-alkenyloxy)arylcarbene and (η^2-alkenylamino)arylcarbene complexes of tungsten.[11] Some of these decompose to cyclopropanes and thus illustrate conversion of carbene–alkene complexes to products compatible with a metallacyclobutane-like species somewhere along the reaction coordinate. Rudler and co-workers have observed cyclopropane products from (η^2-alkenyl)alkoxycarbene complexes of tungsten.[12]

Scheme I



In an effort to probe the structure and reactivity of first-row transition-metal carbene–alkene complexes, we have prepared a chelated carbene–olefin complex of manganese with the allylamino linkage tethering the olefin to the metal carbene in analogy to Casey's tungsten compound.[11b] We report here the synthesis and structure of $(\eta^5\text{-}C_5H_4(CH_3))Mn(CO)[C(C_6H_5)(\eta^2\text{-}NHCH_2CH{=}CH_2)]$.

Results and Discussion

Synthesis of $(\eta^5\text{-}C_5H_4(CH_3))Mn(CO)_2[C(C_6H_5)(NHCH_2CH{=}CH_2)]$ (1). The (allylamino)carbene complex **1**, in which the olefin is not coordinated to the metal, was prepared as indicated in Scheme I.

Both the methoxycarbene **3** and the cationic carbyne complex **4** were prepared according to methods developed by Fischer and co-workers.[13] Addition of excess allylamine to a suspension of the cationic carbyne resulted in instantaneous formation of a dark red solution of **1** accom-

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panied by the precipitation of a white powder. The aminocarbene product 1 was isolated as a moderately air-stable red oil by chromatography on alumina. The complex is soluble in common organic solvents.

Although $(CO)_5W[C(tolyl)(NHCH_2CH{=}CH_2)]$ is readily prepared by treatment of $(CO)_5W[C(tolyl)(OCH_3)]$ with allylamine,[11a,b] 1 cannot be conveniently synthesized by an analogous route. The inertness of 3 compared to $(CO)_5W[C(tolyl)(OCH_3)]$ reflects a relative decrease in the electrophilic character of the manganese carbene carbon vs. the tungsten carbene carbon. The additional carbonyl ligands in the tungsten methoxycarbene complex evidently reduce the metal of $d\pi$ electron density available to the carbene ligand. Conversion of the manganese methoxycarbene to the cationic carbyne 4 greatly enhances the electrophilicity of the α-carbon. Amines and other nucleophiles readily add to the carbyne to generate new carbenes.

The infrared spectrum of 1 shows a typical dicarbonyl pattern with nearly equal intensity absorptions at 1920 and 1850 cm^{-1}. The ^1H NMR of 1 is as expected with several features worth mentioning for comparsion to the ^1H data for the olefin-chelated product to be discussed later. The π-$C_5H_4(CH_3)$ methyl group serves as a nice singlet marker to check for $(\pi\text{-}C_5H_4(CH_3))MnL_n$ contaminants. The four protons of the cyclopentadienyl ring are sufficiently close to one another in chemical shift that they appear as a broad singlet even though they are not equivalent by symmetry. The olefinic protons all resonate between 5 and 6 ppm, with the internal vinylic proton appearing as a complex signal centered near 5.5 ppm.

The ^1H NMR of 1 indicates the presence of isomers. The symmetry-equivalent methylene protons of the alkyl chain appear as two pseudotriplets at 3.01 and 4.26 ppm with an integrated intensity ratio of 2.8:1.0, respectively. The ^{13}C NMR spectrum confirms the presence of isomers. In the region appropriate for the methylene carbon in the alkyl chain, two resonances are observed. The integrated intensity ratio between these signals is 2.7:1.0; respectively. Most of the other carbon resonances appear in a similar pairwise fashion.

Isomerism in this system likely arises from restricted rotation about the carbene carbon–nitrogen bond; such isomerism is well precedented for aminocarbene complexes of various transition metals.[11b,c,14] The ^1H NMR spectrum of the related $(\eta^5\text{-}C_5H_4(CH_3))Mn(CO)_2[C(C_6H_5)(N(CH_3)_2)]$, 5, shows two different *N*-methyl groups with resonances at 2.10 and 3.30 ppm. Heating a solution of 5 in *p*-xylene to 107 °C did not cause coalescence of these signals. This result indicates that the barrier to carbene carbon–nitrogen bond rotation is greater than 21 kcal/mol.

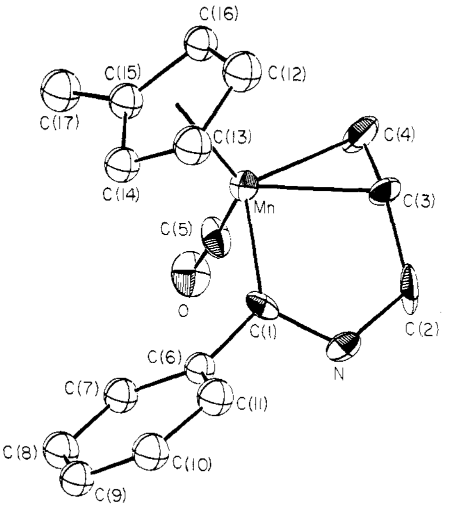

Figure 1. ORTEP drawing and atomic numbering scheme for 2.

Table I. Selected Bond Distances (Å) for 2

Mn-C(1)	1.89 (1)	Mn-C(16)	2.13 (1)
Mn-C(3)	2.10 (1)	O-C(5)	1.21 (1)
Mn-C(4)	2.14 (1)	N-C(1)	1.36 (1)
Mn-C(5)	1.68 (1)	N-C(2)	1.45 (1)
Mn-C(12)	2.15 (1)	C(1)-C(6)	1.49 (1)
Mn-C(13)	2.15 (1)	C(2)-C(3)	1.49 (1)
Mn-C(14)	2.17 (1)	C(3)-C(4)	1.37 (1)
Mn-C(15)	2.16 (1)		

Table II. Selected Bond Angles (deg) for 2

C(1)-Mn-C(3)	79.5 (4)	N-C(1)-C(6)	111.0 (9)
C(1)-Mn-C(4)	111.8 (4)	N-C(2)-C(3)	108.8 (8)
C(1)-Mn-C(5)	84.8 (4)	C(2)-C(3)-C(4)	123 (1)
C(3)-Mn-C(4)	37.7 (3)	Mn-C(5)-O	176.7 (9)
C(3)-Mn-C(5)	103.7 (4)	C(1)-C(6)-C(7)	119.8 (9)
C(4)-Mn-C(5)	87.5 (4)	C(1)-C(6)-C(11)	121.1 (9)
C(1)-N-C(2)	114.0 (8)		

Synthesis of $(\eta^5\text{-}C_5H_4(CH_3))Mn(CO)C(C_6H_5)(\eta^2\text{-}NHCH_2CH{=}CH_2)$ (2). Photolysis of a tetrahydrofuran solution of 1 using a mercury vapor lamp and a Pyrex filter resulted in loss of carbon monoxide and formation of a chelated (allylamino)carbene complex of manganese (2). 2 was isolated as an orange microcrystalline solid after chromatography on alumina. Nicely formed crystals of 2 suitable for an X-ray diffraction study were obtained by slow cooling of a saturated heptane solution. The complex is soluble in common organic solvents, although in alkanes the solubility is low. Complex 2 is extremely air sensitive both in solution and as a powder, but crystals of 2 are somewhat resistant to atmospheric decomposition.

As expected for a monocarbonyl complex, 2 exhibits a single intense absorption (1815 cm^{-1}) in the carbonyl region of the infrared spectrum. A second useful IR observable is the single, sharp absorption at 3300 cm^{-1} which we have assigned to the N–H stretching mode of the chelated aminocarbene.

In the ^1H NMR spectrum of 2, coordination of the alkene moiety shifts the resonances of all the olefinic protons several parts per million upfield relative to those of the free alkene in 1. The terminal olefinic protons appear as simple doublets at 2.02 and 2.17 ppm due to coupling to the remaining vinyl proton (the geminal coupling is negligible), while the internal proton itself is a complex multiplet at 3.33 ppm. Selective homonuclear decoupling experiments were utilized to unambiguously unravel the ^1H spectrum. Formation of the chelate by substitution of a carbon monoxide with the alkene lifts the chemical equivalence of the methylene protons which link the aminocarbene with the olefin, and they appear as widely separated signals centered at 4.46 and 2.48 ppm. Chelation also eliminates the mirror plane present in 1, so the manganese atom becomes a chiral center in 2. As in other chiral manganese compounds which contain the $\eta^5\text{-}C_5H_4(CH_3)$ ligand, each of the four cyclopentadienyl protons appears as a separate signal (3.66, 3.78, 3.92, 4.55 ppm).[15] In the ^{13}C spectrum the olefinic carbon resonances are

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Table III. Least-Squares Planes, Displacement from Mean Plane (Å), and Selected Dihedral Angles (deg)

	Plane 1		
Mn	C(3)	C(4)	
	Plane 2		
Mn	0.001	N	0.001
C(1)	−0.002	C(6)	0.001
	Plane 3		
Mn	A (alkene midpoint)	C(1)	
	Dihedral Angles		
planes 1 and 3 (β)	30.6	planes 2 and 3 (γ)	7.0

Table IV. Atomic Positional Parameters for 2

atom	x	y	z
Mn	−0.0729 (2)	0.0525 (1)	0.2344 (1)
O	0.0295 (9)	0.2019 (5)	0.3795 (6)
N	0.020 (1)	0.1673 (6)	0.0743 (6)
C(1)	−0.110 (1)	0.1442 (7)	0.1272 (8)
C(2)	0.176 (1)	0.1160 (9)	0.1082 (9)
C(3)	0.132 (1)	0.0269 (7)	0.1548 (9)
C(4)	0.181 (1)	0.0031 (8)	0.2609 (9)
C(5)	−0.010 (1)	0.1391 (8)	0.3183 (9)
C(6)	−0.265 (1)	0.1989 (7)	0.0879 (8)
C(7)	−0.335 (1)	0.2556 (1)	0.1593 (9)
C(8)	−0.481 (1)	0.3043 (8)	0.1249 (9)
C(9)	−0.561 (1)	0.2975 (8)	0.0202 (9)
C(10)	−0.499 (1)	0.2419 (8)	−0.0482 (9)
C(11)	−0.352 (1)	0.1905 (8)	−0.0213 (9)
C(12)	−0.303 (1)	−0.0174 (8)	0.1597 (9)
C(13)	−0.180 (1)	−0.0827 (8)	0.2005 (9)
C(14)	−0.147 (1)	−0.0719 (8)	0.3112 (9)
C(15)	−0.245 (1)	0.0010 (8)	0.3403 (9)
C(16)	−0.340 (1)	0.0354 (8)	0.2453 (8)
C(17)	−0.254 (2)	0.0315 (8)	0.4514 (10)

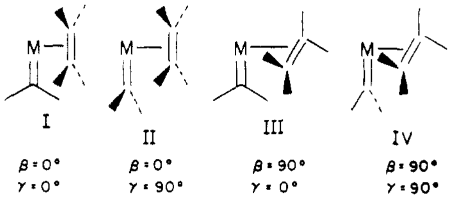
substantially shifted upfield (about 60 ppm) to 58.3 and 59.4 ppm relative to those of the free alkene in 1. Low-field ^{13}C resonances at 286.5 and 241.0 ppm were assigned to the carbene and carbonyl carbons, respectively.

X-ray Crystal Structure of 2. An X-ray crystallograhic study of 2 confirmed its formulation as a manganese–carbene–olefin complex. The nearly octahedral geometry about the manganese center is illustrated in Figure 1, where the atomic numbering scheme is defined. Intramolecular bond distances and angles are reported in Tables I and II, respectively. Selected molecular planes and associated dihedral angles are presented in Table III. Atomic positional parameters are listed in Table IV and crystallographic data and collection parameters are cited in Table V. The bond distances and ligand distribution around the metal are normal for (η^5-cyclopentadienyl)manganese derivatives,[16] and we turn directly to the orientation of the carbene relative to the olefin. In (η^5-C_5H_5)$Mn(CO)_2(C(X)R)$ carbene complexes the plane of the carbene ligand is found near the vertical mirror plane bisceting the two carbonyl ligands.[16a,g] Rotation around the Mn–C carbene bond tends to be rapid on the NMR time scale in accord with calculations indicating that the less favored horizontal orientation is only a few kilocalories per mole above the energy of the vertical carbene orientation.[17]

Table V. Crystallographic Data and Collection Parameters for 2

Crystal Data	
molecular formula	$C_{17}H_{18}MnNO$
formula weight, g/mol	307.28
space group	$P2_1/c$
unit cell parameters	
a, Å	7.936 (2)
b, Å	14.593 (5)
c, Å	12.569 (5)
β, deg	99.08 (3)
vol, $Å^3$	1437.4
ρ(calcd), g/cm^3	1.420
Z	4
Collection and Refinement Parameters	
radiation (wavelength, Å)	Mo $K\alpha$ (0.71073)
linear abs coeff, cm^{-1}	9.57
scan type	$\omega/1.67\theta$
scan width	$1.1 + 0.35 \tan \theta$
bkgd	25% of full scan width on both sides
θ limits	$2.0° \le 2\theta \le 50°$
quadrant collected	$+h,+k,\pm l$
unique data	2641
data with $I \ge 2\sigma(I)$	866
R	0.074
R_w	0.052
largest parameter shift	0.01
no. of parameters varied	121
error in an observn of unit wt	1.56

Chart I. Four Possible Extreme Geometries Available to a Cis Metal Carbene–Alkene



Three angles are required to completely define the geometrical relationship between the carbene and the olefin ligands. In keeping with Casey's angle definitions,[11] we will employ α, β, and γ as depicted below (Chart I). The angle α between the carbene carbon and the midpoint of the olefin describes the gross ligand relationship, i.e., 180° for trans and 90° for cis. Hereafter we will consider only cis complexes. The angle β, independent of carbene rotation, is defined by the dihedral angle between the plane containing the carbene carbon, the metal, and the olefin midpoint (plane 3, Table III) and the plane defined by the MC_2 metal alkene moiety (plane 1, Table III). For parallel M–C carbene and C–C olefin units, β is 0°, while for the perpendicular arrangement β is 90°. The γ angle, independent of olefin rotation, is the dihedral angle between the plane of the carbene ligand (plane 2, Table III) and the carbene carbon–metal–alkene midpoint plane (plane 3, Table III) which measures the twist of the carbene relative to the olefin.

In 2 α was found to be 95.9°, nearly ideally cis, while for $(CO)_4W[C(tolyl)(\eta^2\text{-}NHCH_2CH{=}CH_2)]$ an α value of 76.8°[11b] was reported. The difference in α for the manganese and tungsten complexes may simply reflect the difference in covalent radii between these metals. Casey has suggested that the small allylamino linkage pinches the carbene and alkene together in the tungsten case

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($W{=}C_{carbene}$ = 2.21 Å; W–C_{olefin} = 2.41 Å (average)).[11b] In accord with this hypothesis, the structure of the (butenylamino)tungsten analogue $(CO)_4W[C(tolyl)(\eta^2\text{-}N(CH_3)CH_2C(CH_3)_2CH{=}CH_2)]$, where the ring size has been increased by one atom, exhibits α values of 90.7° and 92.1° for the two independent molecules in the unit cell.[11c] The shorter metal–carbon bonds in the manganese compound accommodate the allylamino chelate nicely with a right angle at the metal center ($Mn{=}C_{carbene}$ = 1.89 Å; Mn–C_{olefin} = 2.12 Å (average)). The effective bite of the chelating allylamino carbene remains nearly constant in the manganese and tungsten complexes (carbene carbon to olefin midpoint 2.84 Å for Mn and 2.87 Å for W).

The olefin is somewhat skewed relative to the metal carbene unit in 2 with β = 30.6°. In contrast the olefin and carbene in $(CO)_4W[C(tolyl)(\eta^2\text{-}NHCH_2CH{=}CH_2)]$ are much closer to perpendicular (β = 77.0°).[11b] In 2 γ = 7.0°; the size of the chelate ring probably restricts γ to relatively small values. In $(CO)_4W[C(tolyl)(\eta^2\text{-}NHCH_2CH{=}CH_2)]$ γ = 25.7° but for the chain extended butenylamino case, γ expands to 42.0°.[11b,c] In summary the geometry of 2 most closely approximates representation I (see Chart I).

The spatial arrangement of the ligands in 2 positions the carbene to compete with CO for dπ electron density. Relative to the vertical carbene orientation, i.e., in the mirror plane as found in $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CPh_2)$,[16g] the carbene in 2 is twisted 37.1° as measured by the angle between the carbene C1–N–C6 plane and the C1–Mn–C_5(midpoint) plane. The olefin π^* orbital stablizes the third dπ orbital of the nest of three created by the rough octahedral geometry, so each of the three filled dπ orbitals is π-bonding relative to CO, carbene, or olefin. If the ring size indeed constrains γ to relatively small values, then the observed orientation with β near 30° should be electronically favored relative to the perpendicular olefin orientation due to maximization of the π-bonding interactions. Comparison of the average ν_{CO} frequency for 1 (1885 cm^{-1}) with the 1815 cm^{-1} value for the single CO in 2 suggests that the olefin is not comparable to CO in π-acidity. We would expect the carbene to be a stronger single-faced π-acid than the alkyl-substituted olefin, even considering the dominant role of the amino lone pair in stabilizing the carbene α-carbon. Nevertheless, since a γ value near 90° would be required in order for the carbene to avoid competition with the cis carbonyl, the steric constraints of the chelate probably inhibit true optimization of electronic factors in 2.

Eisenstein, Hoffman, and Rossi[17c] have calculated a difference in first-row transition-metal carbene–olefin conformational preferences relative to second- and third-row analogues for d^6 metal configurations. In particular they have noted that geometry II (Chart I), the one aligned for metallacyclobutane formation, was lower in energy than geometry I (Chart I) for d^6 $L_4Fe(CH_2)(C_2H_4)$ but higher in energy for similar Mo and W d^6 complexes. Although we observe a difference in the carbene–olefin relationship in 2 relative to Casey's tungsten complex, the only geometry which allows constructive ligand–ligand overlap to overcome the unfavorable dπ orbital competition, II, is not observed in either case. All three remaining isomers alleviate the dπ competition between the carbene and the olefin. The presence of a nitrogen heteroatom in a small chelate may place 2 outside the realm of extended Hückel calculations reported for the model compounds.

Experimental Section

$(\eta^5\text{-}C_5H_4(CH_3))Mn(CO)_2[C(C_6H_5)(NHCH_2CH{=}CH_2)]$ (1). $(\eta^5\text{-}C_5H_4(CH_3))Mn(CO)_2[C(C_6H_5)(OCH_3)]$, **3** (1.56 g, 5.03 mmol), was dissolved in 200 mL of hexane. The solution was cooled to −78 °C. BCl_3 gas was bubbled through the solution until a fluffy yellow solid, **4**, precipitated. The yellow solid was filtered off and then resuspended in a mixture of methylene chloride (30 mL) and hexane (50 mL). Excess allylamine (ca. 5 mL) was added, and the reaction mixture was allowed to warm to room temperature. The reaction mixture quickly turned dark red, and a white solid precipitated. The red supernatant was filtered away from the precipitate; the solvent was removed to afford a red oil. **1** was isolated as a viscous red oil after chromatography on alumina: yield 1.51 g (89.6%); IR (neat) 1920 (s) cm^{-1}, ^{1}H NMR (C_6D_6) (two isomers present in a 2.8:1.0 ratio) δ 1.64 (s, 3 H, $CpCH_3$), 3.01 (t, 5 Hz, 1.53 H, NCH_2 major), 3.95 (br s, 4 H, C_5H_4), 4.26 (t, 5 Hz, 0.54 H, NCH_2 minor), 4.52–5.78 (complex m, 3 H, olefinic protons), 6.32–7.20 (complex m, 5 H, C_6H_5), 8.20 (br s, 1 H, NH); ^{13}C (C_6D_6) (two isomers present) δ 14.1 (q, 128 Hz, $CpCH_3$), 51.4 (t, 134 Hz, NCH_2 major), 53.7 (t, 134 Hz, NCH_2 minor), 84.8 (d, 173 Hz, C_5H_4), 86.2 (d, 174 Hz, C_5H_4), 101.2 (s, C_5H_4 ipso), 116.7 ($C{=}\mathit{C}H_2$ major), 117.9 ($C{=}\mathit{C}H_2$ minor), 121.7 ($\mathit{C}H{=}C$ major), 122.7 ($\mathit{C}H{=}C$ minor), 126.1–133.6 (phenyl region, ortho, meta, para carbons, both isomers), 151.4 (s, ipso phenyl major), 157.5 (s, ipso phenyl minor), 234.5 (br s, CO), 285.0 (s, carbene minor), 287.1 (s, carbene major).

$(\eta^5\text{-}C_5H_4(CH_3))Mn(CO)_2[C(C_6H_5)(N(CH_3)_2)]$ (5). Complex **5** was prepared from **3** (1.20 g, 3.9 mmol) in a manner analogous to that for **1** by using excess gaseous dimethylamine. **5** was isolated as a viscous red oil after chromatography on alumina: yield 1.06 g (84.1%); IR (hexane) 1925 (s), 1855 (s) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.66 (s, 3 H, $CpCH_3$), 2.10 (s, 3 H, NCH_3), 3.30 (s, 3 H, NCH_3), 3.87 (br s, 4 H, C_5H_4), 6.1–7.1 (complex m, 5 H, C_6H_5); ^{13}C (*p*-xylene-d_{10}) δ 14.0 (q, 128 Hz, $CpCH_3$), 45.0 (q, 139 Hz, NCH_3), 49.0 (q, 139 Hz, NCH_3), 84.2 (d, 174 Hz, C_5H_4), 85.8 (d, 177 Hz, C_5H_4), 99.7 (s, C_5H_4 ipso), 120.9, 125.0, 128.0 (phenyl region, ortho, meta, para carbons), 155.0 (s, ipso phenyl), 234.9 (s, CO), 282.8 (s, carbene).

$(\eta^5\text{-}C_5H_4(CH_3))Mn(CO)[C(C_6H_5)(\eta^2\text{-}NHCH_2CH{=}CH_2)]$, 2. An orange solution of **1** (1.51 g, 4.51 mmol) in tetrahydrofuran (400 mL) was transfered to a photolysis chamber and cooled to ca. −30 °C. The solution was irradiated with a mercury vapor lamp (Hanovia, 679A36) through a Pyrex filter for 30 min. A color change from orange to red occurred. The solvent was removed to afford a red oil. **2** was isolated as a pasty orange solid after chromatography on alumina. The solid was washed with cold pentane and dried in vacuo. **2** was recrystallized from hot heptane: yield 0.97 g (70.1%); IR (KBr) (NH) 3300 (s), 1815 (vs) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 1.53 (s, 3 H, $CpCH_3$), 2.02 (d, 10.2 Hz, 1 H, $C{=}CH_2$), 2.17 (d, 7.6 Hz, 1 H, $C{=}CH_2$), 2.48 (dd, 8.8, 12.3 Hz, 1 H, NCH_2), 3.33 (dddd, 10.2, 7.6, 8.8, 6.5 Hz, 1 H, $CH{=}C$), 3.66, 3.78, 3.92, 4.55 (m, 1 H each, C_5H_4), 4.46 (dd, 6.5, 12.2 Hz, 1 H, NCH_2), 7.10–7.40 (complex m, 5 H, C_6H_5), 7.86 (br s, 1 H, NH); ^{13}C NMR (C_6D_6) δ 12.8 (q, 127 Hz, $CpCH_3$, 43.6 (t, 154 Hz, $C{=}\mathit{C}H_2$), 58.3 (t, 134 Hz, NCH_2), 59.4 (d, 147 Hz, $\mathit{C}{=}CH_2$), 84.3, 84.4, 85.6, 88.2 (C_5H_4), 99.2 (s, C_5H_4 ipso), 124.1–129.3 (phenyl region, ortho, meta, para carbons) 152.7 (s, ipso phenyl), 241.0 (s, CO), 286.5 (s, carbene).

Collection of Diffraction Data. A yellow-orange prism of approximate dimensions 0.1 × 0.2 × 0.3 mm was selected, mounted on a glass wand and coated with epoxy cement. Diffraction data were collected on an Enraf-Nonius CAD-4 automated diffractometer.[18] A monoclinic cell was indicated from 25 centered reflections found in the region 16° < 2θ < 26° and refined by least-squares calculations. The cell parameters are listed in Table V.

Diffraction data were collected in the quadrant $+h,+k,\pm l$ under the conditions specified in Table V. Three reflections chosen as intensity standards were monitored every 5 hours and showed no significant (<1.5%) decay. The crystal was checked for orientation after every 300 reflections, and recentering was performed if the scattering vectors varied by more than 0.15°.

Solution and Refinement of the Structure. The structure solution was straightforward from the application of the heavy-atom method. The space group $P2_1/c$ was deduced from systematic absences for $0k0$, $k = 2n$, and $h0l$, $l = 2n$. The manganese atom was located in the three-dimensional Patterson function.

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[18] Programs utilized during solution and refinement were from the Enraf-Nonius structure determination package.

The positions of the remaining non-hydrogen atoms were obtained from subsequent Fourier and difference Fourier calculations.

Least-squares refinement[19] of the 20 non-hydrogen atoms using 737 data with $I > 3\sigma(I)$ and allowing all the atoms to vary isotropically produced unweighted and weighted residuals of 0.072 and 0.067, respectively.[20] The positions of the hydrogen atoms were calcuated by using a C–H distance of 0.95 Å and an isotropic thermal parameter of 5.0. Further full-matrix least-squares refinement using 866 reflections having $I > 2\sigma(I)$ and allowing all the heavy atoms except the cyclopentadienyl and phenyl carbon atoms to vary anisotropically converged with residuals $R = 0.074$ and $R_w = 0.052$.[21] The final difference Fourier map shows no peaks with intensity greater than 0.29 e/Å^3.[22]

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Registry No. 1 (isomer 1), 98689-87-3; 1 (isomer 2), 98757-40-5; 2, 98689-89-5; 3, 34742-22-8; 4, 93756-36-6; 5, 98689-88-4; allylamine, 107-11-9; diethylamine, 124-40-3; carbon, 7440-44-0; nitrogen, 7727-37-9.

Supplementary Material Available: Tables of anisotropic and isotropic thermal parameters, calculated hydrogen positions, complete bond distances and angles, least-squares planes coordinates and dihedral angles, and calculated and observed structure factors (17 pages). Ordering information is given on any current masthead page.

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[19] The function minimized was $\sum w(|F_o| - |F_c|)^2$.

[20] $I = S(C + RB)$ and $\sigma(I) = [2S^2(C + R^2B) + (\rho I)^2]^{1/2}$, where S = scan rate, C = total integrated peak count, R = ratio of scan count time to background count time, B = total background count, and $\rho = 0.01$ is a correction factor.

[21] $R_{\text{unweighted}} = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_{\text{weighted}} = [\sum w\ (|F_o| - |F_c|)^2/\sum wF_o^{\ 2}]^{1/2}$.

[22] Scattering factors were taken from: Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallograpy"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press; Birmingham, England, 1974; Vol. IV, Table 2.2.

Pyrazolyl-Bridged Iridium Dimers. 8. Two-Center, Electrophilic Addition of Activated Acetylenes to Bis(cycloocta-1,5-diene)bis(μ-pyrazolyl)diiridium(I) Leading to a Diiridacyclobutene Configuration: Regular, Parallel Coordination of Methyl Propiolate

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The activated alkynes hexafluorobut-2-yne (HFB), dimethyl acetylenedicarboxylate (DMAD), and methyl propiolate (MPL) react under mild conditions with $[\mathrm{Ir(COD)}(\mu\text{-pz})]_2$ (**1**) to afford 1:1 adducts **2**–**4**, respectively, for which ^{1}H and ^{13}C NMR measurements suggest "parallel" alkyne addition, generating a diiridacyclobutene configuration in which the two metal centers are formally d^7 Ir(II). By contrast the related diiridium(I) complex $[\mathrm{Ir(CO)(PPh_3)}(\mu\text{-pz})]_2$ (**5**) forms a similar adduct (**6**) only with DMAD; with HFB alkyne polymerization occurs, attributed to PPh$_3$ dissociation from **5**. Compounds **3** and **4** have been structurally characterized by using X-ray diffractometry, showing the geometry in each case to resemble that communicated earlier for **2** and substantiating the interpretation of the spectroscopic data. Crystal data for **3**: space group $P2_1/c$, $a = 11.318$ (3) Å, $b = 11.543$ (3) Å, $c = 42.091$ (9) Å, $\beta = 98.07$ (3)°. Crystal data for **4**: space group $P\bar{1}$, $a = 10.983$ (4) Å, $b = 12.585$ (6) Å, $c = 9.862$ (4) Å, $\alpha = 92.96$ (4)°, $\beta = 110.29$ (3)°, $\gamma = 99.41$ (4)°. The adjacent Ir(II) centers in each molecule are spin paired via Ir–Ir bond formation, with single bond distances of 2.633 (2), 2.642 (2) Å (**3**, two independent molecules), and 2.637 (1) Å (**4**), to accommodate which terminal COD ligands are rotated to occupy axial positions at each Ir with alkyne coordination in equatorial sites. Coordination of the unsymmetrical MPL bridging unit is regular with Ir–C$_{\mathrm{MPL}}$ distances equal at 2.094 (mean) Å.

Introduction

Molecular orbital methods have recently been used by Hoffmann and co-workers[2] to develop a comparison in theoretical terms between parallel (A) and perpendicular (B) bridging orientations in binuclear transition-metal acetylene complexes, together with an analysis of possible pathways for interconversion between the two bonding modes. The parallel (dimetallacyclobutene) configuration A has been encountered much less often[2,3] than the alternative B: indeed the former is restricted almost exclusively to products arising from reactions of electron-deficient alkynes (typically R = CF$_3$ or CO$_2$Me), in which

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