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Conformation and Bonding in (η^5-C_5H_5)$(CO)_2$Mn–Carbene Complexes. X-ray Structure Determination of (η^5-C_5H_5)$(CO)_2$MnC(OEt)Ph

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The structure of (η^5-C_5H_5)$(CO)_2$MnC(OEt)Ph has been determined by X-ray diffraction. Cell dimensions are as follows: a = 756.0 (3) pm, b = 722.8 (4) pm, c = 2652 (1) pm, β = 94.11 (4)°, $V = 1445 \times 10^6$ pm^3; space group $P2_1/c$ (Z = 4). R = 0.085 and R_w = 0.068 for the 945 reflections with $F_o \geq 3.92\sigma(F_o)$. The Mn–C(carbene) distance is 186.5 (14) pm. A comparison of all known structures of (η^5-C_5H_5)- or (η^5-$CH_3C_5H_4$)$(CO)_2$Mn–carbene complexes shows that the orientation of the carbene plane approximately in the mirror plane of the (η^5-C_5H_5)$(CO)_2$Mn fragment is more favorable than the orientation perpendicular to it, in agreement with theoretical predictions. However, the structural parameters also show that the conformations found in the structures are largely determined by the substituents at the carbene carbon atom and by crystal packing forces. Therefore, the differences in energy among the different conformations should be small. Because of the high π-donating ability of the (η^5-C_5H_5)$(CO)_2$Mn moiety, the electronic influence of the organic substituents at the carbene carbon upon the metal–carbene carbon bond is weak as long as they are not better π donors than the metal-containing moiety.

Introduction

The importance of transition-metal complexes containing terminal carbene (alkylidene) ligands in organometallic chemistry need not be emphasized. Although their chemical behavior may differ considerably (e.g., electrophilic "Fischer-type"[1] vs. nucleophilic "Schrock-type"[2] complexes as limiting cases), they share a common feature—an sp^2-hybridized carbon atom bonded to a metal by a (partially) double bond. The prerequisite for an understanding of the reactivity of such complexes is to understand their geometries and the nature of the bond between the carbene ligand and the metal-containing moiety. Theoretical studies are able to supply basic concepts but usually are restricted to idealized or simple complexes. The geometries of more complex molecules are obtained by diffraction methods, but interpretation of the structural parameters in terms of bonding can be speculative if it is based on a single structure. However, if one compares the structures of two or more compounds that only differ by a single substituent or ligand, the influence of the replaced group on the bonding situation and the overall geometry can be followed by the changes in structural parameters. In a series of papers we were thus able to show the following from X-ray structure determinations of carbene complexes of the Fischer-type: (i) that regardless of a formal metal–carbon double bond (derived from electron bookkeeping) the actual bond order may even be close to 1[3,4] or larger than 2,[5] depending on the electronic nature of the groups bonded to the carbene carbon atom; (ii) that the three groups (including the metal-containing moiety) bonded to the carbene carbon atom compete with one another for π bonding and that therefore *any* bond length around the carbene carbon atom depends on the π-donating ability of *each* group;[6,7] (iii) that the bond angles at the carbene carbon atom are strongly influenced by steric interactions.[6,8]

The structural study of Cp$(CO)_2$MnC(OEt)Ph (Cp = η^5-C_5H_5, MeCp = η^5-$CH_3C_5H_4$) was undertaken for two reasons. (1) Recently, Kostić and Fenske made detailed predictions about the geometry of Cp$(CO)_2$MnC(OMe)Ph on the basis of molecular orbital (MO) calculations,[13] thus stimulating a structural investigation. (2) The structure of Cp$(CO)_2$MnC(OEt)Ph can be compared with the known structures of Cp- or MeCp$(CO)_2$MnC(X)Ph (X = F,[5] O$^-$,[9] Ph,[10] COPh[11]) and [Cp$(CO)_2$MnC(Ph)]$_2$O.[12] By that comparison the influence of replacing the alkoxy substituent for another one (while keeping the remainder of the molecule intact) on geometry and bonding in carbene complexes with strongly π-donating metal-containing moieties can be studied.

Experimental Section

Crystals of Cp$(CO)_2$MnC(OEt)Ph[14] were obtained by crystallization from a hexane solution. A crystal (0.3 × 0.3 × 0.2 mm) was mounted on a Syntex P2$_1$ automatic four-circle diffractometer equipped with a scintillation counter and a graphite monochromator. Mo K$\bar{\alpha}$ radiation (λ = 71.069 pm) was used for all measurements. Centering and refinement of 15 reflections from different parts of the reciprocal space resulted in the following unit-cell dimensions: a = 756.0 (3) pm, b = 722.8 (4) pm, c = 2652 (1) pm, β = 94.11 (4)°, $V = 1445 \times 10^6$ pm^3 (at −20 ± 2 °C). By systematic absences space group $P2_1/c$ was established; d(calcd) = 1.425 g/cm^3. Diffraction intensities were measured at the same temperature in an ω-scan mode for which the scan range was 0.9°; the scan rate varied as a function of maximum peak intensity from 1.2 to 29.3 min^{-1}. Background radiation was measured on each side of the reflection center for half of the total scan time. A

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Table I. Positional and Thermal Parameters with Their Standard Deviations for $(\pi\text{-}C_5H_5)(CO)_2MnC(OC_2H_5)C_6H_5$

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Mn	0.2906 (3)	0.2339 (3)	0.08908 (7)		C(8)	0.025 (2)	0.341 (2)	0.0762 (5)	2.3 (3)
C(1)	0.405 (2)	0.070 (2)	0.1339 (5)		O(1)	0.533 (1)	−0.058 (1)	0.1307 (3)	
C(2)	0.233 (2)	0.046 (2)	0.0475 (6)		C(11)	0.632 (2)	−0.068 (2)	0.0855 (5)	2.8 (3)
O(2)	0.189 (1)	−0.073 (1)	0.0208 (4)		C(12)	0.759 (2)	−0.227 (2)	0.0929 (5)	3.6 (3)
C(3)	0.477 (2)	0.292 (2)	0.0539 (5)		C(20)	0.345 (2)	0.035 (2)	0.1866 (5)	2.0 (3)
O(3)	0.586 (1)	0.343 (1)	0.0301 (4)		C(21)	0.430 (2)	0.127 (2)	0.2274 (5)	2.0 (3)
C(4)	0.059 (2)	0.302 (2)	0.1290 (5)	2.8 (3)	C(22)	0.367 (2)	0.105 (2)	0.2759 (5)	3.0 (3)
C(5)	0.199 (2)	0.415 (2)	0.1468 (5)	3.0 (3)	C(23)	0.221 (2)	−0.003 (2)	0.2825 (5)	2.6 (3)
C(6)	0.255 (2)	0.520 (2)	0.1070 (5)	2.9 (3)	C(24)	0.137 (2)	−0.094 (2)	0.2422 (6)	2.9 (3)
C(7)	0.144 (2)	0.476 (2)	0.0634 (5)	2.7 (3)	C(25)	0.197 (2)	−0.076 (2)	0.1936 (5)	2.2 (3)

atom	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	2.07 (9)	1.5 (1)	1.71 (8)	0.5 (1)	0.32 (6)	0.1 (1)
C(1)	2.3 (8)	2.8 (8)	1.5 (7)	−0.9 (7)	0.3 (6)	−1.5 (6)
C(2)	2.0 (8)	2.0 (8)	3.2 (9)	1.2 (7)	0.7 (7)	−0.2 (7)
C(2)	4.0 (8)	3.7 (6)	3.8 (6)	0.6 (5)	−0.3 (5)	−1.9 (5)
C(3)	3.0 (8)	1.1 (8)	2.3 (7)	0.4 (7)	−0.7 (6)	0.2 (6)
O(3)	4.1 (7)	3.4 (6)	4.8 (7)	1.1 (5)	2.5 (5)	2.8 (5)
O(1)	2.3 (5)	2.8 (5)	1.8 (5)	0.8 (4)	0.6 (4)	0.6 (4)

atom	x	y	z	atom	x	y	z
H21	0.528	0.208	0.221	H7	0.147	0.536	0.031
H22	0.433	0.166	0.305	H8	−0.070	0.288	0.054
H23	0.176	−0.017	0.315	H111	0.557	−0.091	0.056
H24	0.035	−0.171	0.250	H112	0.698	0.041	0.079
H25	0.137	−0.138	0.164	H121	0.842	−0.190	0.112
H4	0.005	0.214	0.150	H122	0.803	−0.271	0.063
H5	0.246	0.422	0.182	H123	0.706	−0.331	0.109
H6	0.356	0.606	0.109				

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$; B_{ij} in 10^4 pm^2.

Table II. Bond Lengths (pm) and Angles (Deg) with Their Standard Deviations

Bond Lengths

Mn-C(1)	186.5 (14)	C(1)-C(20)	153.6 (19)	C(7)-C(8)	138.7 (20)
Mn-C(2)	179.5 (14)	O(1)-C(11)	147.1 (17)	C(8)-C(4)	145.2 (19)
Mn-C(3)	180.5 (15)	C(11)-C(12)	150.7 (21)	C(20)-C(21)	140.6 (19)
Mn-C(4)	217.7 (14)	C(2)-O(2)	115.9 (18)	C(21)-C(22)	142.4 (20)
Mn-C(5)	217.7 (14)	C(3)-O(3)	114.3 (18)	C(22)-C(23)	138.0 (20)
Mn-C(6)	215.0 (14)	C(4)-C(5)	139.5 (20)	C(23)-C(24)	139.0 (20)
Mn-C(7)	216.7 (15)	C(5)-C(6)	140.2 (20)	C(24)-C(25)	141.5 (20)
Mn-C(8)	217.4 (14)	C(6)-C(7)	143.9 (21)	C(25)-C(20)	140.5 (19)
C(1)-O(1)	135.6 (17)				

Bond Angles

C(1)-Mn-C(2)	90.3 (7)	C(2)-Mn-C(8)	89.1 (6)	C(4)-C(5)-C(6)	108.8 (12)
C(1)-Mn-C(3)	97.8 (6)	C(3)-Mn-C(4)	153.3 (6)	C(5)-C(6)-C(7)	107.6 (13)
C(1)-Mn-C(4)	100.7 (6)	C(3)-Mn-C(5)	122.1 (6)	C(6)-C(7)-C(8)	108.4 (13)
C(1)-Mn-C(5)	94.7 (6)	C(3)-Mn-C(6)	90.4 (6)	C(7)-C(8)-C(4)	107.4 (12)
C(1)-Mn-C(6)	122.0 (6)	C(3)-Mn-C(7)	93.1 (6)	C(8)-C(4)-C(5)	107.8 (12)
C(1)-Mn-C(7)	158.4 (6)	C(3)-Mn-C(8)	126.1 (6)	C(25)-C(20)-C(21)	120.3 (12)
C(1)-Mn-C(8)	136.0 (6)	Mn-C(1)-O(1)	134.6 (10)	C(20)-C(21)-C(22)	119.5 (12)
C(2)-Mn-C(3)	91.1 (7)	Mn-C(1)-C(20)	123.2 (10)	C(21)-C(22)-C(23)	120.0 (13)
C(2)-Mn-C(4)	107.8 (6)	O(1)-C(1)-C(20)	101.7 (11)	C(22) -C(23)-C(24)	120.4 (13)
C(2)-Mn-C(5)	145.1 (6)	Mn-C(2)-O(2)	177.4 (13)	C(23)-C(24)-C(25)	120.9 (13)
C(2)-Mn-C(6)	147.1 (6)	Mn-C(3)-O(3)	173.6 (13)	C(24)-C(25)-C(20)	118.9 (12)
C(2)-Mn-C(7)	108.2 (6)				

reference reflection measured every 50 reflections showed no significant deviation in its intensity. A total of 1926 independent reflections were collected ($2° \le 2\theta \le 48°$). Intensity data were corrected for Lorentz and polarization effects; absorption correction was not applied ($\mu = 6.7$ cm^{-1}). The structure was solved by the heavy-atom method (Syntex XTL); positions of some hydrogen atoms were calculated according to the idealized geometry. Atomic coordinates and temperature factors of the non-hydrogen atoms and a scale factor (116 variables) were refined by full-matrix least squares with 945 structure factors ($F_o \geq 3.92\sigma(F_o)$). Hydrogen atoms were included as fixed-atom contributions ($B_{iso} = 4.0$ Å^2). Final $R_1 = 0.085$ and $R_2 = 0.068$, where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ ($1/w = \sigma^2(F_o) + 0.000\,225F_o^2$). The final positional and thermal parameters are listed in Table I. Table II contains interatomic bond lengths and angles. Table III, the observed and calculated structure factors, is available as supplementary material.

Results and Discussion

Conformation. In $Cp(CO)_2MnCXY$ complexes with two different organic substituents X and Y at the carbene carbon (generally in any (π-arene)$(CO)_2MCXY$ complex), there are three different idealized conformations (A, B, and C in Figure 1), as far as the mutual orientation of the carbene plane and the $Cp(CO)_2Mn$ moiety is concerned. In A the carbene plane is perpendicular to the mirror plane of the $Cp(CO)_2Mn$ fragment with C_s symmetry. In both B and C the carbene plane coincides with the mirror plane. However, B and C differ by the positions of the organic substituents. MO calculations[13,15] have shown that in

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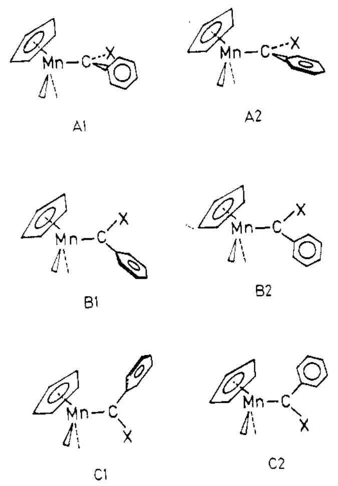

Figure 1. Idealized possible conformations of carbene complexes Cp(CO)$_2$MnC(X)Ph.

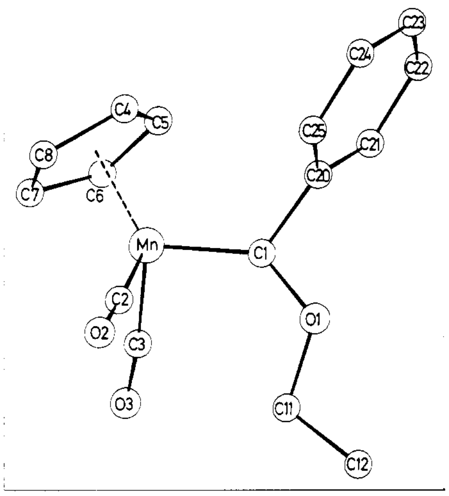

Figure 2. Perspective drawing of Cp(CO)$_2$MnC(OEt)Ph. All hydrogen atoms have been omitted for clarity.

carbene complexes of this type there is a barrier for the rotation of the carbene ligand about the metal–C(carbene) axis and that conformations A, B, and C differ in energy. If one of the organic substituents is a phenyl group, the torsional angle between the carbene and phenyl planes can vary between 0 (A2, B2, C2) and 90° (A1, B1, C1). The limiting conformations are shown in Figure 1. Conformation C2 is very unlikely to occur, since it results in severe steric interactions between the phenyl and cyclopentadienyl rings.

The conformation found in Cp(CO)$_2$MnC(OEt)Ph is best described by C1 (Figure 2). The phenyl ring and the carbene plane are nearly perpendicular (82.4°) to each other. However, the carbene plane is twisted by about 14° relative to the mirror plane of the Cp(CO)$_2$Mn fragment—the angles between the vectors Mn–C(2) and Mn–C(3) and the normal to the carbene plane (Mn, C(1), O(1), C(20)) are 60 (1)° and 31 (1)°.

Kostić and Fenske[13] have calculated the relative energies of the conformations A1, B1, B2, and C1 for Cp(CO)$_2$MnC(OMe)Ph. They found B2 to be the most stable one and B1 to be destabilized by 2, C1 by 14, and A1 by 19 kcal/mol relative to B2.

The apparent discrepancy between the MO calculations and the crystal structure requires some comments.[16] The MO calculations were restricted to four idealized conformations, which certainly do not reproduce the potential surface sufficiently well. Rigorous conformational study would require variations in several structural parameters. Therefore the numerical values for the relative energies are not certain.

If one assumes that the actual energy differences between the various conformations are smaller than the ones calculated by Kostić and Fenske (for Cp(CO)$_2$MnCH$_2$ Schilling, Hoffmann, and Lichtenberger[15] have calculated conformation B (=C) to be more stable than A by 6.2 kcal/mol), than these values reach the magnitude of packing forces. In this case the conformation found in the crystalline state does not necessarily correspond to the conformation that is lowest in energy in the gas phase or in solution.[17]

Comparison of all known structures of Cp- or MeCp(CO)$_2$Mn–carbene complexes[4,5,9–12,19–21] clearly shows that, as predicted by theory,[13,15] the orientation of the carbene plane approximately in the mirror plane of the Cp(CO)$_2$Mn fragment (B and C in Figure 1) is more favorable than the orientation perpendicular to it (A in Figure 1). Conformation A is found in only two structures: Cp(CO)$_2$MnC(menthyl)OMe[21] and MeCp(CO)$_2$MnC(OMe)C(Me)PMe$_3$.[4] In both of these complexes the carbene carbon atom carries bulky substituents, which probably force the carbene plane to orient in a less favorable way with respect to the Cp(CO)$_2$Mn fragment.[22]

If only structures of phenyl-substituted carbene complexes Cp- or MeCp(CO)$_2$MnC(X)Ph are compared with each other (Table IV), one can clearly find a preference for conformation B2,[23] which MO calculations have predicted to be the most stable one for Cp(CO)$_2$MnC(OMe)Ph.[13] One cannot even exclude the possibility that this conformation would be found in crystalline Cp(CO)$_2$MnC(OMe)Ph. The fact that Cp(CO)$_2$MnC(OEt)Ph has a conformation different from those of most of the other Cp(CO)$_2$MnC(X)Ph complexes and the fact that some Cp(CO)$_2$Mn–carbene complexes even adopt conformation A prove that the conformation easily can be adjusted to steric or crystal lattice requirements. This means that the differences in energy between conformations A, B, and C, in particular between B and C, cannot be large.

The same should be true for Bz(CO)$_2$Cr–carbene complexes (Bz = η^6-C$_6$H$_6$). MO calculations predict a reorientation of the carbene plane (A in Figure 1) in comparison with Cp(CO)$_2$Mn–carbene complexes.[13] Indeed, conformation A2 is found in crystalline Bz(CO)$_2$CrC(OMe)Ph.[6] However, this is the only known structure of a carbene complex of this kind, and one cannot exclude the possibility of finding conformations B or C (Figure 1) in later structure determinations, provided that substituents with different steric or packing properties are bonded to the carbene carbon.

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(16) I acknowledge the valuable discussions with N. M. Kostić, whose comments concerning the MO calculations are given in this paragraph.

(17) See Ref 7 and 18 for further examples.

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(22) In MeCp(CO)$_2$MnC(OMe)C(Me)PMe$_3$[4] the Mn–C("carbene") bond order is near 1. Therefore the difference in energy among the various conformations should be much smaller than in the other carbene complexes.

(23) In [Cp(CO)$_2$MnC(O)Ph]NMe$_4$[9] there may be cation–anion interaction, which cause the anion to adopt a certain conformation. In Cp(CO)$_2$MnCPh$_2$ one phenyl ring must adopt conformation C1 if the other one adopts B2.

Table IV. Comparison of Structural Parameters in Carbene Complexes MeCp- or $Cp(CO)_2MnC(X)Ph$[a]

	X					
	OEt	Ph[10]	C(O)Ph[11]	O[12]	O^-[b,9]	F[5]
bond distances (pm)						
Mn-C (carbene)	186.5 (14)	188.5 (2)	188 (2)	187 (2)[c]	196 (2)	183.0 (5)
mean Mn-C(CO)	180 (1)	178.8 (2)	174 (2)	178 (2)[c]	178 (3)	179.0 (6)
mean Mn-C(C_5H_5)	217 (1)	217.2 (2)	217 (2)	216 (2)[c]	217 (4)	214.8 (6)
bond angles (Deg)						
Mn-C (carbene)-C(C_6H_5)	123 (1)	130.6 (1)[d] 116.7 (1)[e]	132 (1)	129 (1)[c]	121 (2)	136.4 (4)
Mn-C (carbene)-X	135 (1)		116 (1)	119 (1)[c]	125 (2)	117.5 (4)
C(C_6H_5)-C(carbene)-X	102 (1)	112.7 (2)	111 (1)	112 (2)[c]	114 (2)	106.1 (4)
dihedral angles (Deg)						
carbene plane/phenyl plane	82.4		4.7	49.8/41.5	50.3	6.5
carbene plane/C_5H_5 plane	80.7		84.7	80.0/72.9	57.6	89.5
phenyl plane/C_5H_5 plane	23.3		85.5	84.2/76.8	16.2	89.4
conformation (according to figure 1)	C1	B2[d]/C1[e]	B2	between B1 and B2	between A and C	B2

[a] Parameters not published in the original papers were calculated from the atomic coordinates. [b] Mean values from two independent molecules in the asymmetric unit. [c] Mean values from both halfs of $[Cp(CO)_2MnC(Ph)]_2O$. [d] Phenyl ring in the mirror plane of the $Cp(CO)_2Mn$ fragment. [e] Phenyl ring perpendicular to the mirror plane of the $Cp(CO)_2Mn$ fragment.

Bonding. By comparison of the structures of $(CO)_5CrC(OMe)Ph$[24] and $Bz(CO)_2CrC(OMe)Ph$ we have shown[6] that in the latter complex the Cr–C(carbene) bond order is much higher than in the former, because of the better π donation from $Bz(CO)_2Cr$ than from $(CO)_5Cr$. By the same argument, the Mn–C(carbene) bond order also should be high in $Cp(CO)_2Mn$–carbene complexes. Both types of carbene complexes should exhibit similar chemical behavior. By means of its high back-bonding ability $Cp(CO)_2Mn$ supplies sufficient electron density to the carbene carbon, and thus π-donating organic substituents at the carbene carbon are not necessary for the stability of such complexes. As a matter of fact, $Cp(CO)_2MnCXY$ complexes have been prepared in which both X and Y are bonded to C(carbene) via a carbon atom.[25] Correspondingly $(CO)_5MCXY$ complexes (M = Cr, Mo, W) are very unstable or cannot be prepared.

One structural consequence of the π-donating ability of the $Cp(CO)_2Mn$ fragment is that in $Cp(CO)_2MnC(OEt)Ph$ the C(1)–O(1) distance (136 (2) pm) is longer than in alkoxycarbene complexes in which the alkoxy groups serve as π-donating substituents. One can conclude from the C(carbene)–O bond length that in $Cp(CO)_2MnC(OEt)Ph$ the ethoxy group poorly, if at all, competes with the $Cp(CO)_2Mn$ moiety for π bonding with the carbene carbon. A further structural consequence of the high π-donating ability of the $Cp(CO)_2Mn$ fragment is the fact that the Mn–C(1) bond length (186.5 (14) pm) is the same as in most of the $Cp(CO)_2Mn$–carbene complexes studied so far and is not significantly influenced by the nature of the organic substituents. Thus, in the $Cp(CO)_2MnC(X)Ph$ series (Table IV) there are no significant changes in the Mn–C(carbene) distances, if X = Ph or COPh is replaced by potentially π-donating substituents such as X = OEt or an oxo bridge. The contrary would be expected in $(CO)_5MCXY$ complexes. Only if the π-donating ability of one organic substituent considerably exceeds that of the $Cp(CO)_2Mn$ fragment is lengthening of the Mn–C(carbene) bond (i.e., decrease in the Mn–C(carbene) bond order) observed (as in $[Cp(CO)_2MnC(O)Ph]^-$,[9] 196 (2) pm or in $MeCp(CO)_2MnC(OMe)C(Me)PMe_3$,[4] 199 (1) pm). On the other hand, the Mn–C(carbene) bond may be shortened by hyperconjugation in special cases; e.g., in $Cp(CO)_2MnC(F)Ph$[5] it is 183.0 (5) pm.

The different conformations do not significantly influence the Mn–C(carbene) bond lengths (see Table IV[26]). However, there is some influence on the bond angles at the carbene carbon. In conformations B and C the largest Mn–C(carbene)–substituent angles are observed for the substituent, which is anti to the Cp ring (phenyl in conformation B and X in conformation C). Thus, the Mn–C(1)–O(1) angle in $Cp(CO)_2MnC(OEt)Ph$ (135 (1)°) is comparable to the Mn–C(carbene)–C(phenyl) angles in the carbene complexes having conformation B2 (see Table IV). These angles seem to be determined by steric interactions between the CO ligands and the substituents at the carbene carbon which point in the same direction. Depending on the different environments of the two possible locations for the organic substituents at the carbene carbon the Mn–C(carbene)–C(phenyl) angles are 10–15° smaller in complexes with conformation C1 than in complexes with conformation B. It is foreseeable that in $Cp(CO)_2MnC(X)Ph$ the preferred conformation will largely depend on the steric requirements of the substituent X relative to that of a phenyl group.

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Supplementary Material Available: Table III, listing of the observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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(24) Mills, O. S.; Redhouse, A. D. *J. Chem. Soc. A* **1968**, 642–647.

(25) Caulton, K. G. *Coord. Chem. Rev.* **1981**, *38*, 1–43 and references cited therein.

(26) Though the compounds with the longest Mn–C(carbene) bond distances[4,9] tend toward conformation A, this conformation does not *cause* bond lengthening. This is obvious from the comparison with the Mn–C(carbene) distance of 189 (2) pm in $Cp(CO)_2MnC(menthyl)OMe$, the other complex having conformation A.