

How realistic are alternating C–C-bond lengths in *s-cis*-1,3-butadiene transition metal complexes? †

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Received 17th October 2001, Accepted 18th December 2001

First published as an Advance Article on the web 13th February 2002

A crystallographic redetermination of bis(*s-cis*-1,3-butadiene)monocarbonylmanganese showed that the earlier reported C–C bond lengths of the butadiene fragments are probably *artefacts* caused by pseudo symmetry problems. The problems of pseudo symmetry have been solved and the correct absolute structure has been assigned during the refinement of the structure in the non-centrosymmetric tetragonal space group $P4_2m$. This redetermination yielded balanced C–C distances for the complexed butadiene fragments. The molecular structure of the title compound has also been investigated by DFT-quantum chemical calculations [Becke3LYP/6-31+G(d) (C, H, O); 6-31G(f) (Mn)]. The typical understanding of bonding of butadienes to transition metal complexes and the experimental geometric parameters are in impressive agreement with the quantum chemical calculations. The problems discussed can also be expanded to molecular structures of isotypical complexes and similar pentamethylcyclopentadienyl transition metal complexes that crystallise in the space group $P4_2m$ with the molecules located on a $C_{2v}(mm2)$ site.

Introduction

In the mid-sixties the first bis(*s-cis*-1,3-butadiene) complexes of rhodium¹ and iridium² [(C₄H₆)₂MCl, M = Rh (**1**), Ir (**2**)] were synthesized and subsequently characterized by single crystal X-ray diffraction. The synthesis, spectroscopic investigation and structural characterisation of bis(*s-cis*-1,3-butadiene)monocarbonyliron (**3**)^{3,4} and bis(*s-cis*-1,3-butadiene)monocarbonylmanganese (**4**)^{5,6} followed.

In addition, the butadiene complexes of the ‘early’ transition metals have been intensively studied. There exist some precise structures of corresponding butadiene complexes allowing a detailed view of the bonding situation in these complexes.⁷ However, the series of isotypical complexes **1–4** with crystallographic symmetry $C_{2v}(mm2)$ show remarkably long central C–C-distances and relatively short terminal C–C-distances in the *s-cis*-1,3-butadiene ligands. Comparing the structures of these complexed butadiene fragments with the gas phase structure of free *s-cis*-1,3-butadiene determined by electron diffraction⁸ and the *ab initio* theoretically calculated structure,⁹ it is surprising that complexation should lead to longer terminal C–C-distances than expected but to an unchanged central C–C-bond (Table 1).

The first synthesis and characterisation of a bis(*s-cis*-butadiene) transition metal complex with crystallographic point symmetry 1 [bis(*s-cis*-1,3-butadiene)trimethoxyphosphine-manganese (**5**)] was achieved by Harlow *et al.*¹⁰ With respect to the standard uncertainties this complex shows balanced C–C-distances in both crystallographically independent butadiene ligands. However, the large standard uncertainties in complexes **1–4** lead, on the one hand, to discussions about the observed alternating bond lengths in all of these structures and, on the other, to discussions about the balanced bond lengths in **5**. Neither of these factors can be well described at present.

Table 1 Summary of C–C-bond lengths of bis(*s-cis*-butadiene)metal complexes and free *s-cis*-butadiene (all values in Å, values in square brackets corrected for thermal motion)²¹

	C2–C3	C3–C3'	Ref.
(C ₄ H ₆) ₂ RhCl (1)	1.38(2)	1.45(2)	1
(C ₄ H ₆) ₂ IrCl (2)	1.41(1)	1.47(1)	2
(C ₄ H ₆) ₂ FeCO (3)	1.43(2)	1.46(1)	3
(C ₄ H ₆) ₂ MnCO (4)	1.39(1)	1.46(1)	6
	1.404(3) ^a	1.411(4) ^a	
	[1.419(3)]	[1.427(4)]	
	1.411(2) ^b	1.418(3) ^b	
	[1.418(2)]	[1.426(3)]	
	1.4196 ^c	1.4243 ^c	
(C ₄ H ₆) ₂ MnP(OMe) ₃ (5)	1.404(4)	1.405(4)	10
	1.407(4)		
	1.414(3)	1.408(3)	
	1.409(4)		
<i>s-cis</i> -C ₄ H ₆	1.342(2)	1.463(3)	8

^a 293 K. ^b 150 K. ^c DFT calculation.

Experimental

General procedures

The reaction and all manipulations were performed under a nitrogen atmosphere by using standard Schlenk techniques. The solvent was purified, dried, and kept under nitrogen prior to use, according to procedures known from the literature.¹¹

Preparation

Bis(*s-cis*-1,3-butadiene)monocarbonylmanganese can be synthesized by the direct photo reaction of Mn₂(CO)₁₀ with butadiene. Purification by recrystallisation from n-pentane leads to blue–green, needle shaped crystals.

† Dedicated to Professor H.-G. Kuball on the occasion of his 70th birthday.

X-Ray crystallography

The refinement was carried out in the non-centrosymmetric space group $P\bar{4}2_1m$ (absolute axis assignment), starting from the known structural model.¹² A converged refinement of this model to the global minimum was only possible if the anisotropic displacement parameters for all non-hydrogen atoms, the hydrogen positions and the absolute structure were taken into account.¹³ However, a refinement of the inverse absolute structure leads to wrong bond lengths in the *s-cis*-butadiene ligands and finally ends in a local minimum. The difficulties in finding the global minimum arise from the fact that in this case the electron density distribution of the inverted structure is very similar to the density of the true structure. These problems can only be handled by the application of an adequate refinement and data collection strategy (e.g. carrying out a data collection strategy that also measures the weak reflections very precisely and uses an appropriate weighting scheme).^{14,15} A refinement of the structure as a hypothetical inversion twin (TWIN/BASF combination of the SHELX-system) led to the same results for the true structure but showed a significantly better convergence.

Crystal data for (C₄H₆)₂COMn. Needle shaped crystals, size: 0.78 × 0.16 × 0.13 mm³, $M_r = 191.13$, tetragonal, space group $P\bar{4}2_1m$.

$T = 293$ K. $a = 7.8215(8)$, $b = 7.2234(8)$ Å, $V = 441.90(8)$ Å³, least-squares refinement of the lattice constants: 5000 quasi-centred reflections, $Z = 2$, $\rho_{\text{calc.}} = 1.436$ Mg m⁻³, $\mu = 1.43$ mm⁻¹, Stoe-IPDS diffractometer, Mo-K α radiation ($\lambda = 0.71073$ Å), ϕ -scan, 4831 measured reflections in the range of $6.22 < \theta < 26.99^\circ$, 490 unique intensities, minimizing of $\sum w(F_o^2 - F_c^2)$ with $w = 1/[\sigma^2(F_o^2) + (0.0353P)^2 + 0.0296P]$ and $P = (F_o^2 + 2F_c^2)/3$, 43 refined parameters, $R1 = 0.0202$, $wR2 = 0.0527$, $S = 1.040$, Flack-parameter: $-0.01(3)$, $-0.14 < \Delta\rho < +0.23$ e Å⁻³.

$T = 150$ K. $a = 7.729(3)$, $c = 7.167(2)$ Å, $V = 428.1(3)$ Å³, $Z = 2$, $\rho_{\text{calc.}} = 1.483$ Mg m⁻³, $\mu = 1.478$ mm⁻¹, Siemens P4 diffractometer equipped with a LT2-cooling device, Mo-K α radiation ($\lambda = 0.71073$ Å), ω -scan, 2007 measured reflections in the range of $4.69 < \theta < 25.46^\circ$, 445 unique intensities, minimizing of $\sum w(F_o^2 - F_c^2)$ with $w = 1/[\sigma^2(F_o^2) + (0.0169P)^2 + 0.03P]$ and $P = (F_o^2 + 2F_c^2)/3$, 44 refined parameters, $R1 = 0.0128$, $wR2 = 0.0328$, $S = 1.092$, Flack-parameter: $-0.01(2)$, $-0.16 < \Delta\rho < +0.22$ e Å⁻³.

CCDC reference numbers 158318 ($T = 150$ K) and 158319 ($T = 293$ K).

See <http://www.rsc.org/suppdata/dt/b1/b109454h/> for crystallographic data in CIF or other electronic format.

Results and discussion

The C–O bond length and all Mn–C distances are in good agreement with the values determined before. The manganese centre is surrounded by two *s-cis*-1,3-butadiene ligands, each in a η^4 -type coordination mode (Fig. 1). Remarkable differences between the presented structure and that known from the literature were found for the C–C-distances of the *s-cis*-1,3-butadiene ligands. With respect to the estimated standard uncertainties they must now be interpreted as balanced (Table 1). This finding fits very well with the concept of bonding and back bonding of transition metals to olefinic ligand systems.¹⁶

The optimised geometry of a density functional calculation¹⁷ [Becke3LYP/6-31+G(d) (C, H, O); 6-31G(f) (Mn)]¹⁸ leads to very good agreement between the structural parameters from the optimised molecular geometry and the values found by X-ray crystal structure determination. A frequency calculation was performed to ensure that the optimized geometry represented a minimum on the potential energy surface. The typical understanding of bonding of butadienes to transition metal complexes is in impressive agreement with the quantum chemical calculations. Fig. 2 (right) shows a molecular orbital which represents a bond. Electrons are shifted from the HOMO

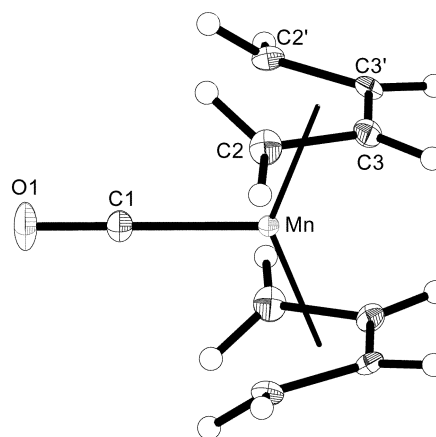


Fig. 1 Diagram of the molecular structure of **4** in solid state at 150 K; 50% ellipsoids. Radii of the hydrogen atoms are arbitrarily chosen; Mn–C1 1.810(2), Mn–C2 2.141(2), Mn–C3 2.0790(13) Å; C2–C3–C3' 118.88(8)°.

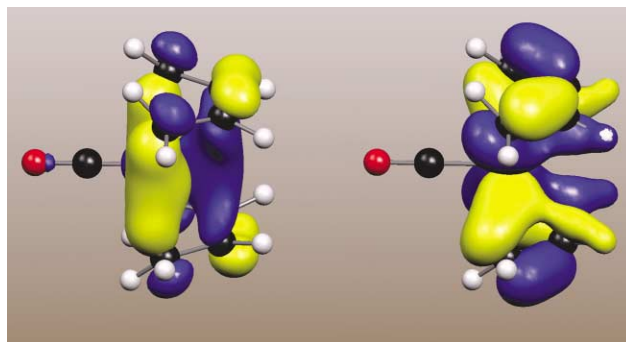


Fig. 2 Two selected occupied molecular orbitals of complex **4**.²⁰ An imaginary separation into fragment orbitals leads to the following interpretation. (Right) Electrons are shifted from the HOMO of the butadiene fragments to the manganese centre and (left) electrons are shifted from the manganese into the LUMO of the butadiene fragments.

of the isolated butadiene fragments to the manganese centre. This weakens the terminal C–C bonds while strengthening the central C–C-bond. Fig. 2 (left) shows a MO which represents back bonding in which electrons are formally shifted from the manganese centre into the LUMO of the isolated butadiene fragments. This has the same effect on the bond lengths as described above. Considering these results alternating C–C-bond lengths in butadiene in the isotypically complexes **1–4** are an *artefact* that arises from problems during the structure refinement. Nearly balanced C–C bond lengths are also plausible from our DFT quantum chemical calculation (Table 1). The fact that the structures of all isotypically complexes **1–4** suffer from pseudo symmetry producing C–C bond length variations has been substantiated by the refinement of the structure of the rhodium complex, **1**, based on published diffraction data. This structure also shows more equilibrated C–C bonds in the revised refinement.

To expand these problems of structure refinement to other classes of compounds an enquiry was made to the Cambridge Crystallographic Data Centre for molecular structures crystallizing in the space group $P\bar{4}2_1m$ with the molecules located at a C_{2v} ($mm2$) site. Beside others, pentamethylcyclopentadienyl transition metal complexes were found in which the bonding is theoretically proven but show analogous artificial distortion of the cyclopentadienyl ligands.¹⁹

Conclusion

For the title compound it was shown that strong distortions of the molecular geometry are possible even when quality

diffraction data are used, the *R*-values are good and the space group is correctly chosen. The serious refinement problems lead to results with wrong geometric parameters and small estimated standard uncertainties that invite incorrect interpretations. It is shown that the problems discussed can also be expanded to molecular structures of isotypical complexes and similar pentamethylcyclopentadienyl transition metal complexes that crystallize in the space group $P\bar{4}2_1m$ with the molecules located on a C_{2v} ($mm2$) site. This special combination of molecular symmetry and space group symmetry inevitably leads to wrong structures in routine structure determination work. The DFT calculations allow a detailed view of the bonding of olefinic systems to transition metal complexes and verify the experimental results.

Acknowledgements

We thank Dr Joachim Krakehl for crystals of bis(*s-cis*-1,3-butadiene)monocarbonylmanganese and Dr Stuart Pace for reading the manuscript. Finally, the Universitätsrechenzentrum der Heinrich-Heine-Universität Düsseldorf is acknowledged for providing computing time.

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