

$[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}]_2(\mu\text{-OC})_2[\text{cpMo}(\text{CO})_2]_2$ (cp = $\eta^5\text{-C}_5\text{H}_5$): A Compound with Linear Co-ordination of Titanium to a Bridging Carbonyl and a d⁶–d⁶ [cpMo(CO)₂]₂ Fragment

Eric J. M. de Boer,^a Jan de With,^a and A. Guy Orpen^b

^a Shell Research B.V., Badhuisweg 3, 1031 CM Amsterdam, The Netherlands

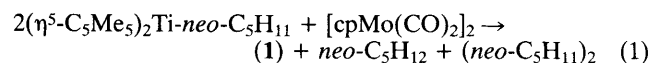
^b Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

Reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti-}neo\text{-C}_5\text{H}_{11}$ with $[\text{cpMo}(\text{CO})_2]_2$ (cp = $\eta^5\text{-C}_5\text{H}_5$) yields the title compound (1); X-ray analysis of (1) shows a 4e (σ, π) Ti–O interaction, resulting in a novel linear co-ordination of titanium to a bridging carbonyl and a new geometry of a $[\text{cpMo}(\text{CO})_2]_2$ fragment caused by a d⁶–d⁶ (Mo–Mo) electron count.

Compounds in which CO is activated by co-ordination of a Lewis acid to the oxygen of a metal-co-ordinated CO ligand (bi-functional activation) are well-known.¹ A number of compounds containing cyclopentadienyl (cp) complexes of the early transition and lanthanide metals (*e.g.* cp₂M, with M = Ti, Zr, Hf, Yb) co-ordinated to metal carbonyls have been structurally characterized. In these complexes the CO ligand binds *via* oxygen to the cp₂M unit and *via* carbon to one or three other metal atoms; all show a *non-linear* M–O–C arrangement. We have now characterized a *linear* M–O–C arrangement in the compound $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}]_2(\mu\text{-OC})_2[\text{cpMo}(\text{CO})_2]_2$ (1), a new and remarkable compound, which shows the theoretically predicted geometry of a $[\text{cpMo}(\text{CO})_2]_2$

dimer with the so far unknown d⁶–d⁶ (Mo–Mo) electron count.

Compound (1) is prepared in about 50% yield as a green crystalline compound by reaction of $(\text{C}_5\text{Me}_5)_2\text{Ti-}neo\text{-C}_5\text{H}_{11}$ with $[\text{cpMo}(\text{CO})_2]_2$ in benzene at room temperature, according to equation (1). Compound (1) is paramagnetic and is a



2:1 adduct of $(\text{C}_5\text{Me}_5)_2\text{Ti}$ and $[\text{cpMo}(\text{CO})_2]_2$, showing $\nu(\text{CO})$ at 1872 and 1351 cm^{−1}. It reacts with CCl₄ to give $(\text{C}_5\text{Me}_5)_2\text{-TiCl}_2$ and $[\text{cpMo}(\text{CO})_2]_2$. To characterise (1) more fully a low-temperature X-ray structure analysis† was carried out.

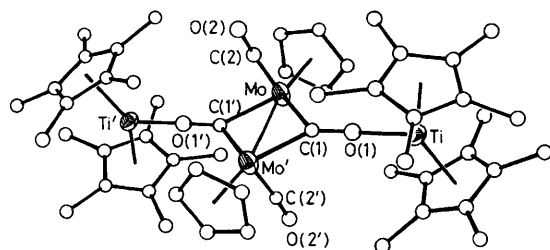


Figure 1. Molecular structure of (1). Bond distances (Å) and angles (°). Mo–C(1) 2.047(5), Mo–C(2) 2.005(8), C(2)–O(2) 1.163(11), C(1)–O(1) 1.271(7), O(1)–Ti 1.929(4), Mo–Mo' 2.647(1), Mo'–C(2) 3.116(7); Ti–O(1)–C(1) 177.9(4), O(1)–C(1)–Mo 138.8(4), O(1)–C(1)–Mo' 140.4(4), Mo–C(1)–Mo' 80.8(2), C(1)–Mo–C(1') 99.2(2).

† Crystal data for (1): C₅₄H₇₀Mo₂O₄Ti₂, *M* = 1070.8, monoclinic, space group *P*2₁/*c*, *a* = 10.652(5), *b* = 12.819(8), *c* = 18.110(9) Å, β = 110.20(4)°, *U* = 2 426(2) Å³, *Z* = 2, *D*_c = 1.47 g cm^{−3}, *F*(000) = 1107.7, *T* = 220 K, graphite monochromated X-radiation, λ = 0.71069 Å, μ(Mo–Kα) = 8.50 cm^{−1}. Intensity data were collected on a Nicolet R3m at ca. 220 K for 4<2θ<50; current residual *R* = 0.062 for 3449 unique, absorption corrected, observed *I*>3σ(*I*) data. Molecules of (1) lie at crystallographic inversion centres (at midpoint of Mo–Mo' bond). The atomic co-ordinates of this work are available, on request, from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

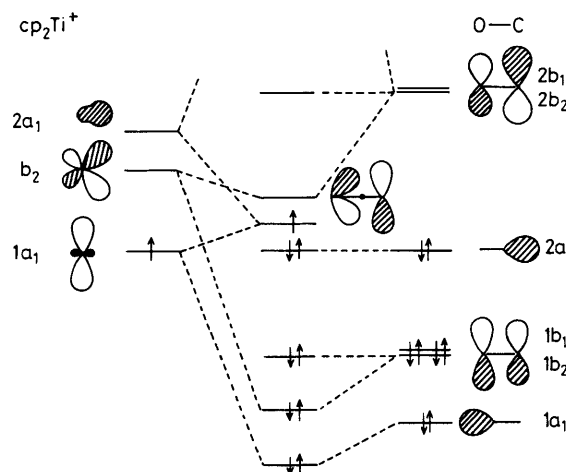
The structure of (1) is given in Figure 1 with some important angles and distances. (1) is a centrosymmetric compound in which two $(C_5Me_5)_2Ti$ fragments are co-ordinated onto the $[cpMo(CO)_2]_2$ fragment *via* the oxygen atoms of two $(Mo-Mo)$ bridging CO ligands. The plane formed by the two (C_5Me_5) -ring centroids, Ti, and O is nearly perpendicular to the plane formed by the two titanium atoms and the atoms of the $Mo_2-(\mu-CO)_2$ core: the dihedral angle is 93.5° .

There are two remarkable features in the structure of (1): (i) a linear Ti-O-C chain; and (ii) the rearrangement of the four semi-bridging CO ligands in $[cpMo(CO)_2]_2$ to two bridging and two terminally co-ordinated CO ligands. These structural observations may be explained in a coherent fashion with the aid of the theoretical work of Hoffmann *et al.*^{2,3} Of importance to (i) the linearity of the Ti-O-C chain is the observation that both the Ti-O and the C-O bond are of approximate bond order two. This indicates a 4e interaction between Ti and O using $2a_1$ - and b_2 -acceptor orbitals from the cp_2Ti fragment and a σ - and a π -donor orbital from oxygen (Scheme 1). Most effectively this is achieved with an sp-hybridization on oxygen, offering the possibility for a strong Ti-O π -interaction in a symmetrical co-ordination along the z-axis,⁴ which in this linear arrangement, will lead to optimal overlap for Ti-O and C-O. An additional benefit is the creation of a low-lying acceptor orbital at the bridging carbonyl by combination of the b_2 -orbital with an antibonding O-C orbital.⁵ This orbital lies in the plane bisecting the (C_5Me_5) -ring planes and can readily interact with the filled orbitals of the $[cpMo(CO)_2]_2$ fragment.^{6†} In the crystal structure of (1) an almost optimal orientation of the $(C_5Me_5)_2Ti$ unit relative to the $Mo_2-(\mu-CO)_2$ plane exists for this interaction.

The structural stability of (1) must be seen as a co-operation of the 4e (σ, π) interaction with the backbonding from the Mo_2 fragment to the isocarbonyl. Although we cannot quantify the relative contributions of these two interactions, it may well be that the carbon being μ_2 *i.e.* the backbonding in the Mo_2 unit, is the most important interaction.

The change of geometry (ii) of the $[cpMo(CO)_2]_2$ fragment is related to the electron count of the molybdenum atoms. In line with its paramagnetic behaviour, (1) is best described by considering it as a $(C_5Me_5)_2Ti^{III}$ derivative [and this implies an electron transfer from $(C_5Me_5)_2Ti^{II}$ (from $d^2 \rightarrow d^1$) to the $[cpMo(CO)_2]_2$ fragment [from $d^5 \rightarrow d^6$ (Mo)]. By simple extension of the theoretical arguments of Hoffmann *et al.* for the various geometries of $cp_2M_2(CO)_4$ species, the d^6-d^6 (Mo-Mo) electron count will cause a change in geometry with the observed dibridged structure with two terminal CO ligands as the most favourable in this case.³

Recently, Bercaw reported the reaction of $(C_5Me_5)_2Zr$ with $[cpFe(CO)_2]_2$.⁷ In this case the Zr^{II} is formally oxidized to Zr^{IV} and the electrons supplied to the $[cpFe(CO)_2]_2$ are used to form a carbon-carbon bond between two CO molecules.



Scheme 1. Qualitative orbital interaction diagram for (1). On the left hand side are the cp_2M fragment orbitals, on the right hand side the orbitals of the bridging CO ligand; local C_{2v} -symmetry is assumed. Of the π - and π^* -orbitals only the orbitals of b_2 symmetry are depicted. The C-O σ -interaction and empty high-energy orbitals are omitted. The negative charge resides on the $[cpMo(CO)_2]_2$ fragment.

Although the difference in metal frameworks will not be the single cause, the disparity in products from the two reactions may reflect the important role of the metal carbonyl fragment in determining the course of the reaction.

Received, 17th June 1985; Com. 842

References

- 1 R. T. Edidin, B. Longato, B. D. Martin, S. A. Matchett, and J. R. Norton, in 'Organometallic Compounds Synthesis, Structures, and Theory,' ed. B. L. Shapiro, Texas A. M. University Press, Texas, p. 260; and references cited therein.
- 2 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.
- 3 E. D. Jemmis, A. R. Pinhas, and R. Hoffmann, *J. Am. Chem. Soc.*, 1980, **102**, 2576.
- 4 Theory predicts an asymmetric (not along the z-axis) co-ordination for a simple $2e$ σ -donor R in $cp_2Ti^{III}R$ (ref. 2). However, the only structure known for such a complex involves a sterically demanding group $R = 2,6-Me_2C_6H_3$, see G. J. Olthof and F. van Bolhuis, *J. Organomet. Chem.*, 1976, **122**, 47, which may mask this electronic effect. A $4e(\sigma, \pi)$ interaction similar to that in (1) occurs in *e.g.* $cp_2Ti^{III}OR$ ($R = 2,6-Bu_2,4-MeC_6H_2$), see B. Cetinkaya, P. B. Hitchcock, M. F. Lappert, S. Towoni, J. L. Atwood, W. E. Hunt, and M. L. Zawrotko, *J. Organomet. Chem.*, 1980, **188**, C31.
- 5 The π -donor interaction of the oxygen with Ti produces an acceptor orbital at the isocarbonyl carbon atom which is nearly pure carbon p in character (as it would be in a $\mu-CCH_2$ or $\mu-CMe$ complex): R. E. Colborn, D. L. Davies, A. F. Dyke, A. Endesfelder, S. A. R. Knox, A. G. Orpen, and D. Plaas, *J. Chem. Soc., Dalton Trans.*, 1983, 2661.
- 6 (a) S. Merola, R. A. Gentile, G. B. Ansell, M. A. Moderick, and S. Zentz, *Organometallics*, 1982, **1**, 1731; (b) D. M. Hamilton, Jr., W. S. Willis, and G. D. Stucky, *J. Am. Chem. Soc.*, 1981, **103**, 4255; (c) G. Schmid, V. Batzel, and B. Stutte, *J. Organomet. Chem.*, 1976, **113**, 67.
- 7 D. H. Berry, J. E. Bercaw, A. J. Jircitano, and K. B. Mertes, *J. Am. Chem. Soc.*, 1982, **104**, 4712.

† Cf. the following bond lengths and angles.

	Ti-O/Å	C-O/Å	Ti-O-C/°	Ref.
$cp_2Ti(THF)(\mu-OC)Mocp(CO)_2$	2.14	1.20	135.4	6a
$(C_5Me_5)_2TiMe(\mu-OC)Mocp(CO)_2$	2.06	1.21	144.3	6b
$cp_2TiCl(\mu-OC)Co_3(CO)_9$	1.94	1.22	164.7	6c
(1)	1.93	1.27	178.4	