Journal of Organometallic Chemistry, *478* (1994) 29–36

Possibility of bond stretch isomerism in $[Cp(CO)_2M]_2(\mu\text{-}E)$ complexes ($M = Mn$, Re, Cr and W; $E = S$, Se and Te); a molecular orbital study

Eluvathingal D. Jemmis, P.N.V. Pavan Kumar [1] and G. Narahari Sastry

School of Chemistry, University of Hyderabad, Central University, P.O., Hyderabad 500 134 (India)

(Received September 23, 1993)

Abstract

Extended Hückel calculations have been carried out on $[Cp(CO)_2M]_2(\mu\text{-}E)$ complexes ($M = Mn$, Re, Cr and W; $E = S$, Se and Te) in linear, bent and triangular geometries. The possibility of double well potential and consequent "bond stretch isomerism" in these complexes is analyzed. All the complexes with a 38 valence electron count (VEC) are calculated to have a minimum corresponding to the triangular geometry. The Mn and Cr complexes with a tellurido bridge have an additional minimum for the bent geometry; only the bent structure is known experimentally. The triangular isomers of these two complexes are marginally higher in energy, but separated by substantial barriers. The other M_2E combinations studied adopt a triangular geometry. The difference in the behaviour between these complexes is explained by the fragment molecular orbital approach and by considering the atomic radii of the M and E species. Single point *ab initio* calculations using the LANL1MB basis set on $[cp(CO)_2M]_2(\mu\text{-}E)$ ($M = Mn$ and Re; $E = S$, Se and Te) confirm the relative energy orderings produced by the extended Hückel calculations. The relation between the M–E bond orders and bond lengths and the extent of Main Group d-orbital participation is also analyzed. It is predicted that complexes with a VEC of 36 and 40 should adopt linear and bent geometries, respectively.

Key words: Chromium; Tungsten; Manganese; Rhenium; Chalcogens; Molecular orbital calculations

1. Introduction

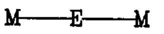
The number of structural patterns involving transition metals and bare Main Group elements is rapidly increasing [1,2]. With two transition metal fragments (M) around a central main group element (E) only three basically different arrangements are possible: linear (**1**), bent (**2**) and triangular (**3**). Table 1 presents a list of well characterized MEM structures with for each the valence electron counts (VEC), M–E–M angle (θ), M $\cdots$ M, and M–E distance. There is a general relationship between the VEC and the structural type. Thus 36 VEC species [3–10] are linear, 38 VEC species [11–15] exist in both bent and triangular forms, and 40 VEC series [16–19] are bent. The existence of two different structures which differ in respect of one interatomic distance as in **2** and **3** for the same number of electrons constitutes bond stretch isomerism [20]. Bond stretch isomerism is not yet unequivocally established in transition metal chemistry [21] but is known for the M_2E complexes. There are two well characterized examples of 38 VEC complexes that show bent and triangular structures respectively; thus $[Cp^*(CO)_2Mn]_2Te$ (**4**) is bent [11] whereas its Re analogue, **5**, is triangular [14]. The factors that control these preferences are not well understood. Studies in transition metal organometallic chemistry have revealed various cases in which a change of the metal within the same VEC leads to a different structural type [22]. What is the role of the Main Group element or the transition metal in preferring one structure over the others even when the number of valence electrons remains constant? The current interest in bond stretch isomerism [23] has prompted us to examine this question. We have attempted to analyse the electronic structures of complexes **1**, **2** and **3**, and especially to understand the factors that impart stability to the bent and the triangular structures with a 38 VEC. Results of extended Hückel [24] and Fenske-Hall [25,26] calculations were reported previously for the linear MEM structures and

---

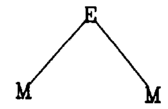
Correspondence to: Professor E.D. Jemmis.

[1] Present Address: Bio-Numeric Pharmaceutical Inc., Suite 1250, 8122, Datapoint Dr, San Antonio, TX 78229, USA.

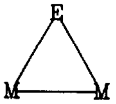
0022-328X/94/$7.00
SSDI 0022-328X(93)24289-H



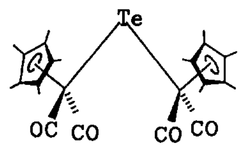
1



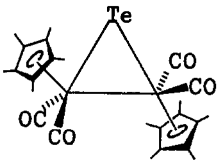
2



3



4



5

showed that an increase of VEC from 36 to 38 leads to a change from linear to bent geometry.

We begin with the description of the electronic structure of $[Cp(CO)_2Mn]_2Te$ (4) a 38 valence electron complex. The comparison of Mn and Re complexes and reasons for their adopting two different structures are then considered. A study with different M and E combinations (M = $CrCp(CO)_2$, $MnCp(CO)_2$, $WCp(CO)_2$ and $ReCp(CO)_2$; E = S, Se and Te) but with the same number of electrons has been carried out to provide a general understanding. The Fragment Molecular Orbital approach [27] within the extended Hückel formalism [28] is used in this study. Single point *ab initio* SCF MO calculations with the LANL1MB basis set [29,30] on bent and triangular geometries of

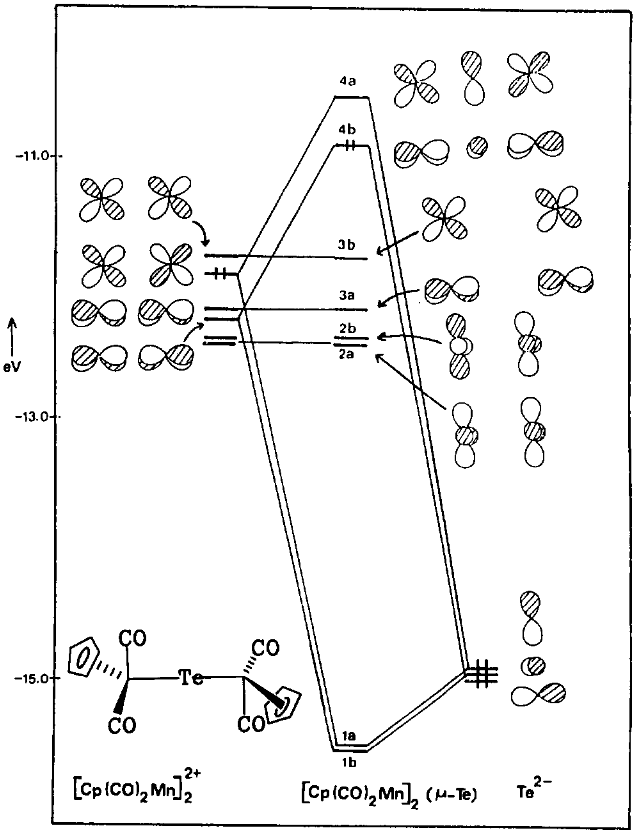


Fig. 1. Orbital Interaction Diagram of $[Cp(CO)_2Mn]_2^{2+}$ and Te^{2-}. The interaction of one of the p orbitals of Te^{2-} with the out of phase combination of the σ-type orbital of $[Cp(CO)_2Mn]_2^{2+}$ is not shown here.

TABLE 1. Important geometric parameters and VEC for the M_2E complexes. Bond lengths in Å and bond angles in degrees

Complex	Type	M–E	M–M	θ	VEC	Ref.
$S[CrCp(CO)_2]_2$	1	2.074	4.148	174.7	36	3, 4
$S[Co(np_3)]_2$	1	2.128	4.156	180.0	36	5
$S[Ni\{(P_3)\}]_2^{2+}$	1	2.034	4.068	180.0	36	5
$S[Mo(HB(Pz)_3)(CO)_2]_2$	1	2.181	4.362	180.0	36	6
$S[Mo(HB(Me_2Pz)_3)(CO)_2$	1	2.200	4.400	180.0	36	6
$S[Mo(CN)_6]_2$	1	2.172	4.344	180.0	36	7
$Se[CrCp(CO)_2]_2$	1	2.209	4.418	180.0	36	8, 9
$Se[Mo(HB(Pz)_3)(CO)_2]_2$	1	2.323	4.646	180.0	36	5
$Se[V(CO)_3(dppe)]_2$	1	2.298	4.596	180.0	36	10
$Te[V(CO)_3(dppe)]_2$	1	2.500	4.963	165.9	36	10
$Te[MnCp^*(CO)_2]_2$	2	2.459	4.338	123.8	38	11
$S[ReCp^*(CO)_2]_2$	3	2.381	2.946	76.4	38	12
$Se[ReCp^*(CO)_2]_2$	3	2.493	3.033	74.9	38	13
$Te[ReCp^*(CO)_2]_2$	3	2.679	3.140	71.7	38	14
$Se[Rh(Cp(CO)_2]_2$	3	2.440	2.755	68.7	38	15
$Te[CrCp^*(CO)_3]_2$	2	2.807	4.792	117.2	40	16
$S[WCp^*(CO)_3]_2$	2	2.531	4.530	127.0	40	17
$Se[FeCp^*(CO)_2]_2$	2	2.449	4.138	115.3	40	18
$Se[Re(PMe_3)_2(CO)_3]_2$	2	2.650	4.495	116.0	40	19

Mn and Re complexes with S, Se and Te bridge are used as a check on the electronic structure and energies obtained from the extended Hückel calculations. Extended Hückel calculations have also been carried out for 36 VEC and 40 VEC complexes with the above M and E combinations. Wherever possible structural parameters available from X-ray diffraction studies have been used in the calculations. The variation of the geometry along the reaction coordinate is indicated in the Appendix.

2. Results and discussion

The molecular orbitals of $[Cp(CO)_2Mn]_2(\mu\text{-Te})$, in the linear geometry, are constructed from the fragment orbitals of $[Cp(CO)_2Mn]^{2+}$ and Te^{2-} (Fig. 1). The $[Cp(CO)_2M]$ dimer orbitals are constructed from those of the well known $Cp(CO)_2M$ fragment [31]. The two Cp rings are placed *trans* to each other and hence the overall symmetry of the molecule is only C_2. The orbital energy pattern is similar to that for linear systems that have been studied in detail previously [24–26]. With a 38 VEC, only one of the two π^* orbitals, 4b, is occupied. The two π^* orbitals form an e_g set in D_{4h} symmetry. Due to the lower symmetry, C_2, we observe splitting of the energy levels of the π^* orbitals, but the HOMO–LUMO energy difference is very small. Any geometrical change that lowers the anti-bonding interaction is favoured for the 38 and 40 VEC species. The 38 VEC complexes may even adopt a linear structure with a triplet ground state. We do not consider this possibility further in view of the limitation of the methods employed. Bending decreases the antibonding character in the in-plane π^*-orbital, 4a. The Re complex, **5**, is found to have a triangular geometry with the two Cp rings *trans* to each other. In the Mn complex, **4**, the two Cp rings are in *cis* conformation. If the two Cp rings are *cis*, or if their centroids are coplanar to the MEM plane, the triangular geometry involves steric interactions. Therefore, the two Cp rings are kept *trans* to each other and are approximately perpendicular to the MEM plane during bending. The nature of the potential energy surfaces does not depend substantially on the Cp ring orientations in going from linear to bent geometries.

Figure 2 shows the frontier orbitals of $(Cp(CO)_2Mn)_2(\mu\text{-Te})$ in linear, bent and triangular geometries. The stabilization of the in-plane π^* orbital (4a) is the only significant change on going from the linear to the bent structure. The nonbonding orbital, 3b, becomes an M···M σ^* orbital. However, the two metals are still at a nonbonding distance in the bent geometry.

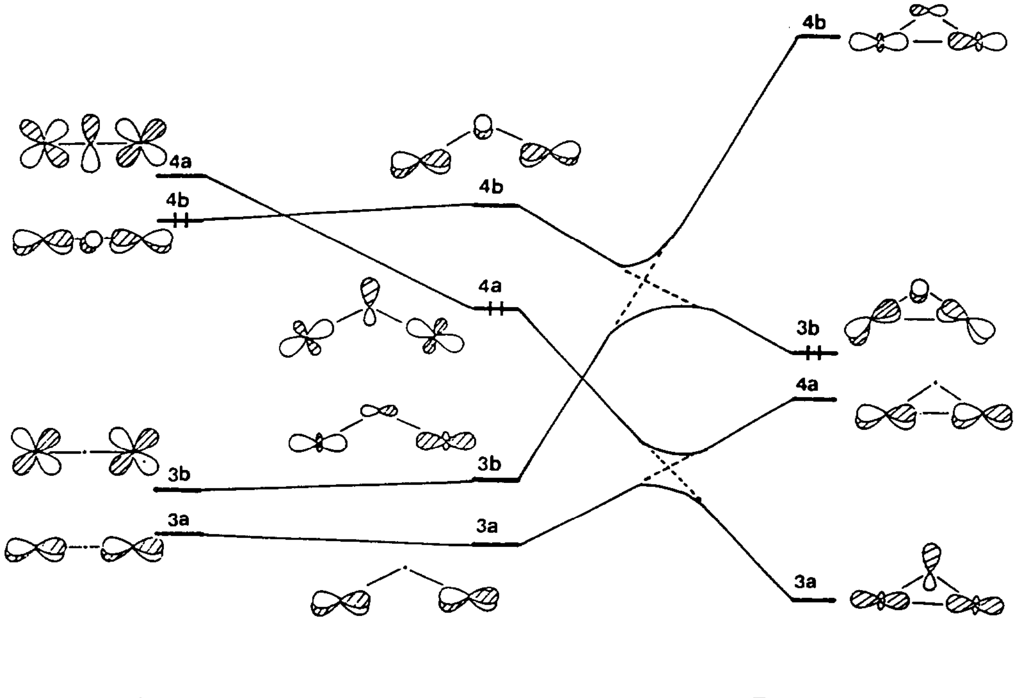


Fig. 2. Schematic representation of the variation of the energy and shape of frontier molecular orbitals of $[Cp(CO)_2M]_2(\mu\text{-E})$ in linear, bent and triangular geometries.

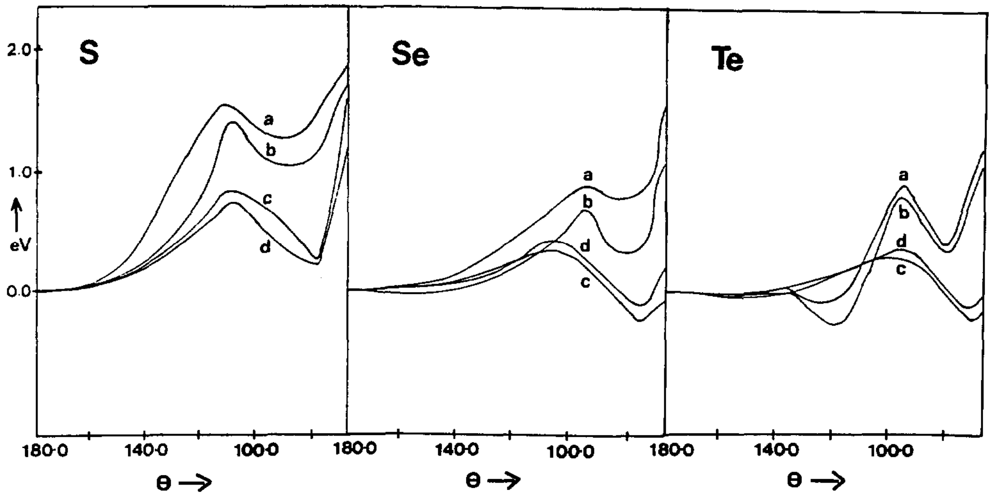


Fig. 3. The plots of the sum of one electron energies of the 38 VEC complexes as a function of the M–E–M angle, θ, in degrees: a = $[Cp(CO)_2Cr]_2(\mu\text{-}E)^{2-}$; b = $[Cp(CO)_2Mn]_2(\mu\text{-}E)$; c = $[Cp(CO)_2Re]_2(\mu\text{-}E)$; d = $[Cp(CO)_2W]_2(\mu\text{-}E)^{2-}$.

The changes are very large on going from a bent to a triangular geometry (Fig. 2). The M–E–M out of plane π^*-orbital, 4b, is occupied. A metal–metal π^*-orbital, 3b, after an avoided crossing with 4b, becomes a metal–metal σ^*-orbital (LUMO) in the triangular geometry. The M–E π^* orbital, 4b (linear), after the avoided crossing, retains antibonding interaction with E but gains M–M π-bonding interaction in the triangular geometry. The other M–E π^* orbital, 4a (linear), becomes stabilized during the bending.

A plot of the sum of one electron energies shows two minima for $[Cp(CO)_2Mn]_2(\mu\text{-}Te)$ complex, corresponding to the bent ($\theta = 124°$) and the triangular ($\theta = 80°$) structures (Fig. 3). The bent structure is shown to be more stable than the triangular structure by about 0.75 eV. The corresponding plot for the Re complex shows a minimum corresponding to the triangular structure only. There is virtually no change in the energy on going from the linear to the bent structure (from $\theta = 180°$ to $120°$). These results are in agreement with the experimental observation that the Re complex has a triangular geometry and the Mn complex a bent geometry. We must seek an explanation of this behaviour from MO theory.

The electronic structures of Mn and Re complexes are qualitatively similar in linear, bent and triangular geometries, but the variation in the energy of the individual orbitals is different. We trace the change in the slopes of the frontier orbitals, 4a, 4b, 3a and 3b along the bending coordinate to the fragment levels themselves. The interaction between $[Cp(CO)_2Mn]_2$ and Te fragment orbitals is stronger than that between

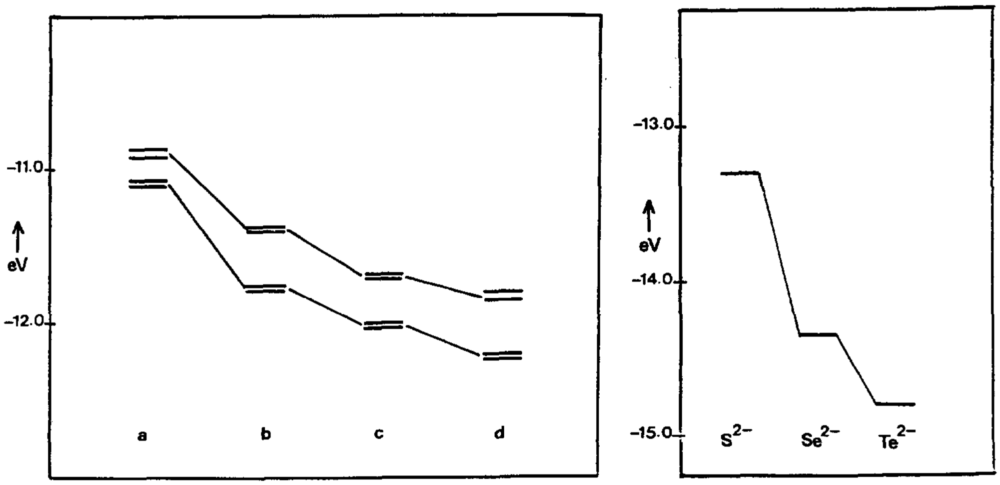


Fig. 4. Correlation of energy levels of $[Cp(CO)_2M]_2^{2+}$ fragment orbitals (a = W; b = Re; c = Cr; d = Mn) and E^{2-} (E = S, Se and Te) orbitals.

$[Cp(CO)_2Re]_2$ and Te fragment orbitals in the linear geometry, because the Mn fragment orbitals are closer in energy to the Te orbitals (Fig. 4). Since the Mn–Te interaction in the Mn complex is stronger, orbital coefficients on Te in the π^* MOs, 4a and 4b, are larger, leading to stronger antibonding interactions. Thus the stabilization of the in-plane π^* orbital, 4a, on going from the linear to the bent geometry is larger for the Mn complex. Fig. 2 indicates that an M–E–M π^*-orbital must be filled in the triangular geometry. The stronger interactions between M and E lead to a higher antibonding interaction in the triangular geometry. Operating along with this is the subtle effect of the M–E distance, in its turn a consequence of the atomic radius of E. When the M–E distance is large, even in the bent geometry the M–M distance falls in the nonbonding range. The destabilizing interaction from 3b is not very large, so that there could still be a minimum at this geometry. The antibonding interaction becomes substantial for a short M–E distance. Thus, a larger E atom is more suitable for a double well potential with minima at bent and triangular geometries.

A systematic study with different M and E combinations [M = $[Cp(CO)_2Mn]$, $[Cp(CO)_2Cr]$, $[Cp(CO)_2Re]$, $[Cp(CO)_2W]$ and E = S, Se, Te] with a 38 VEC (Fig. 3) reveals the ME combinations for which a double well potential and consequent bond stretch isomerism may be anticipated. Figure 4 gives the Fragment Molecular Orbital energies for $[Cp(CO)_2M]_2$ and E for all the combinations studied. The potential energy surfaces for the bending of Cr and Mn complexes are similar. The Re and W complexes form another comparable set (Fig. 3). This clustering is to be expected from the fragment orbital energy levels (Fig. 4). The energy difference is lowest for the Cr and S combination, and highest for the W and Te combination. Both miss the minimum corresponding to the bent geometry, but for different reasons. In the Cr complex, the Cr–S bonds are so short that the two metals are already at a repulsive distance in the bent geometry and hence there is no minimum. A change of E from S to Te gives rise to a minimum corresponding to the bent geometry (Fig. 3). The W–Te combination is similar to that of the Re–Te combination. The reasons for the absence of the minimum are also the same. In this case a change of metal is required since the W–Te interaction is too weak. Alternatively, a more diffuse E atom should give rise to a minimum corresponding to the bent geometry. The metals having weaker interactions with E orbitals, *e.g.* W and Re, prefer closed structures. This is reflected in Fig. 4. All the Re and W complexes have a lower minimum corresponding to triangular geometry than do those of the Mn and Cr complexes. Only the Mn and Cr complexes with a tellurido bridge has a double well potential energy surface for all the combinations.

TABLE 2. Relative energies (in kcal/mol) of bent and triangular geometries obtained from single point *ab initio* calculations using the LANL1MB basis set

E	M = $MnCp(CO)_2$		M = $ReCp(CO)_2$	
	bent	triangular	bent	triangular
S	5.4	0.0	47.6	0.0
Se	1.4	0.0	36.1	0.0
Te	0.0	3.1	40.1	0.0

Ab initio calculations on the LANL1MB basis have been performed for bent and triangular geometries of Mn and Re complexes with S, Se and Te bridges [29,20]. The ordering of the energy levels is similar to that indicated by the extended Hückel calculations for both bent and triangular geometries. For the Mn complex the bent structure is more stable than the triangular structure by 3.1 kcal/mol. For the Re complex, the triangular structure is more stable than the bent one by 40.1 kcal/mol. Table 2 shows the relative energies of the two isomers. It indicates that the Re complex shows a strong preference for the triangular structure. For the Mn complexes the minima corresponding to the bent and the triangular geometries are comparable. The experimentally observed Mn–Te complex has a bent geometry; it is very likely that the triangular structure could also be prepared. The barrier to interconversion of the two structures should be fairly high as indicated by Molecular Orbital energy pattern (Fig. 3), implying the possibility of bond stretch isomerism. The reported sulfido, selenido and tellurido bridged Re complexes have the triangular form (Table 1). The energy differences between the bent and triangular forms of S and Se bridged Mn (or Cr) complexes are small. Thus, these are potential candidates for observation of bond stretch isomerism, examples of which are yet to be observed experimentally in transition metal chemistry.

Extended Hückel calculations have also been performed for various metal ring combinations (M=$WCp(CO)_2$, $ReCp(CO)_2$, $CrCp(CO)_2$ and $MnCp(CO)_2$; E = S, Se and Te) with 36 and 40 VECs. The required electron count is obtained by appropriately placing the charges on the complexes. All the complexes with a 36 VEC are found to be linear, since the two π-orbitals are occupied and the corresponding π^*-orbitals vacant. For complexes with 40 VEC both the π^* orbitals are occupied in the linear geometry. The triangular structure is not favoured because a high lying M–M σ^* MO, 2b, is occupied (Fig. 2). Hence only bent structures may be preferred for these complexes. The plot of the sum of the one electron energies show only one minimum for 40 VEC complexes, that corresponds to the bent geometry. Similar curves generated with different M and E combinations with a 36 VEC are depicted in Fig. 5. In all the cases the energy corresponding to the linear geometry is the lowest. However, there is also a minimum in most of the examples corresponding to the triangular geometry. But this minimum is much higher in energy than that for the linear structure. Figure 2 explains this feature of PES with a 36 VEC. There must be a HOMO–LUMO crossing in the passage from a linear to a triangular structure with a 36 VEC. The HOMO–LUMO energy difference is very small in the triangular geometry. Therefore bond stretch isomerism is unlikely to be observed for 36 VEC MEM complexes.

Linear complexes with a 36 VEC have short M–E bond lengths (2.034 Å for Ni–S; 2.128 Å for Co–S) corresponding to a triple bond. Bent species with a 38 VEC have bond lengths (2.459 Å for Mn–Te) corresponding to a double bond. Bent structures with a 40 VEC have only single (2.807 Å for Cr–Te) M–E bonds. The triangular structures with a 38 VEC retain partial double bond character and have bond lengths (2.679 Å for Re–Te) between those of the 38 VEC bent species and the 40 VEC bent species (Table 1). The indicators of bond multiplicity and the expectation from conventional electron counting schemes often do not agree [32]. The criterion for the former in transition metal complexes is often the bond lengths and for the latter it is the number of electrons in the bonding and the antibonding orbitals. In 36 VEC linear complexes, in addition to the M–E σ-bond there are two 3c–2e π-bonds, 1a and 1b (Fig. 1) which effectively give one π-bond for each M–E. Mealli and Sacconi have shown that there is considerable d-orbital participation in the linear structure [23]. With the inclusion of d orbitals on E, two more π bonding orbitals are occupied (otherwise these are non bonding, 3a and 3b in the linear geometry). This accounts for the triple bond between M and E in linear structure with a 36 VEC [24]. The extra two electrons in a 38 VEC species go into the antibonding π^* orbitals, 4b, in the linear geometry. This should actually decrease the M–E bond order only by half, but the bond lengths correspond to a double bond. In this case the comparison is between the linear 36 VEC species and the bent 38 VEC species. When we go from 38 to 40 VEC (both in the bent form) only two electrons are added to the MEM π^* orbitals, but two bonds are broken. This goes against the general concept of bond order.

The dilemma of two electrons in the antibonding orbitals breaking two bonds is not very difficult to understand if one looks at the bonding and antibonding character of MEM π- and π^*-orbitals, respectively. The two π^*-orbitals, 4a and 4b (linear), have almost equal coefficients on M(0.47) and E(0.55), but the π-orbital has very small coefficients on M(0.11) compared to those on E(0.59). The M–E antibonding interaction in π^*-orbitals is stronger than the bonding in π-orbitals in these complexes. Effectively, the occupation of one π^* orbital cancels two π-bonds formed by weak π-bonding orbitals. We find that the bonding in the bent and the triangular structures also benefits

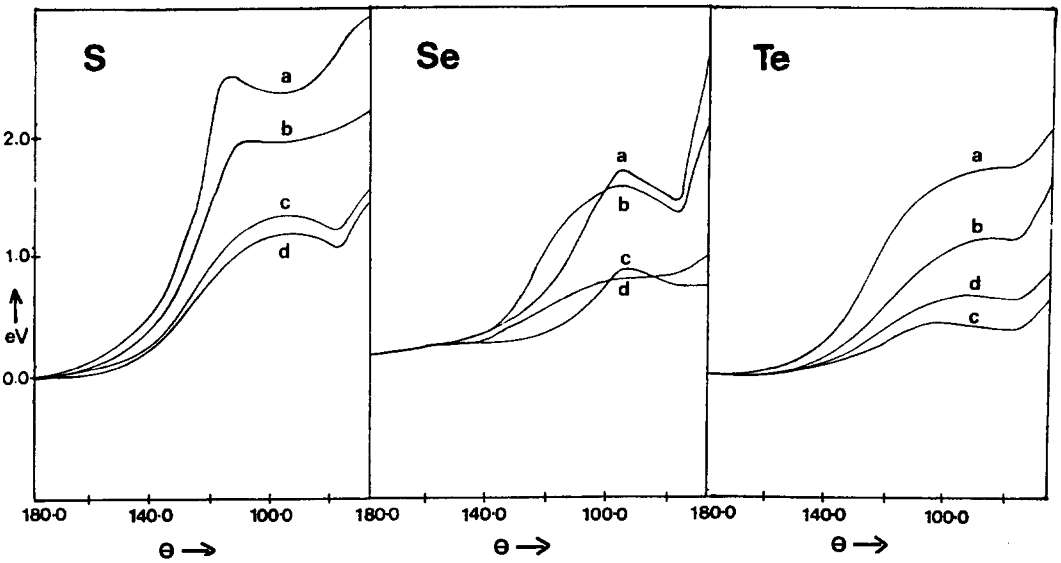


Fig. 5. The plots of the sum of one electron energies of the 36 VEC complexes as a function of the M–E–M angle, θ, in degrees: a = $[Cp(CO)_2Cr]_2(\mu\text{-}E)$; b = $[Cp(CO)_2Mn]_2(\mu\text{-}E)^{2+}$; c = $[Cp(CO)_2Re]_2(\mu\text{-}E)^{2+}$; d = $[Cp(CO)_2W]_2(\mu\text{-}E)$.

from the Main Group d-orbital participation. However the trends obtained with and without d-orbitals are the same. Similar observations have been made earlier [33].

3. Conclusions

A Molecular Orbital study of the complexes $[Cp(CO)_2M]_2(\mu\text{-}E)$ (M=Mn, Re, W and Cr; E = S, Se and Te) indicates that a suitable M and E combination provides a double minimum on the potential energy surface. The Mn (or Cr) complex with a tellurido bridge has two minima, corresponding to the bent and triangular forms. The two minima are energetically comparable and are separated by a high barrier. The structure with the bent geometry has been observed experimentally and attempts to prepare the triangular structure should be rewarding. Similar bond stretch isomerism involving bent and triangular structures is unlikely in the remaining M and E combinations considered.

Acknowledgments

GNS thanks the Council of Scientific and Industrial Research, New Delhi, for a Senior Research Fellowship.

References

1 W.A. Herrmann, *Angew. Chem., Int. Ed. Engl. 25* (1986) 56 and references therein.
2 K.H. Whitmire, *J. Coord. Chem., 17* (1988), 95.
3 T.J. Greenhough, B.W.S. Kolthammer, P. Legzdins and J. Trotter, *Inorg. Chem., 18* (1979) 3543.
4 L.Y. Goh, T.W. Hambley and G.B. Robertson, *J. Chem. Soc., Chem. Commun.,* (1983) 1458.
5 C. Mealli, S. Midollini and L. Sacconi, *Inorg. Chem., 17* (1978) 632.
6 S. Lincoln, S.-L. Soong, S.A. Koch, M. Sato and J.H. Enemark, *Inorg. Chem., 24* (1985) 1355.
7 C. Potvin, J.-M. Manoli, J.-M. Bregeault and G. Chottarrd, *Inorg. Chim. Acta, 72* (1983) 103.
8 W.A. Herrmann, J. Rohrmann, H. Noth, Ch.K. Narula, I. Bernal and M. Draux. *J. Organomet. Chem., 284* (1985) 189.
9 L.Y. Goh, C. Wei, C. Sinn and E.J. Sinn, *J. Chem. Soc., Chem. Commun.,* (1985) 462.
10 N. Albrecht, P. Hubener, U. Behrens and E. Weiss, *Chem. Ber., 118* (1985) 4059.
11 W.A. Herrmann, C. Hecht, M.L. Ziegler and B. Balbach, *J. Chem. Soc., Chem. Commun.,* (1984) 686.
12 M. Herberhold, D. Reiner, K. Ackermann, U. Thewalt and T. Debaerdemaeker, *Z. Naturforsch., 39b* (1984) 1199.
13 M. Herberhold, B. Schmidknoz, U. Thewalt, A. Razavi, H. Schollhorn, W.A. Herrmann and C. Hecht, *J. Organomet. Chem., 229* (1986) 213.
14 W.A. Herrmann, C. Hecht, E. Herdtweck and H.-J. Kneuper, *Angew. Chem., Int. Ed. Engl., 26* (1987) 132.
15 H. Brunner, N. Janietz, W. Meier, J. Wachter, E. Herdtweck, W.A. Hermann, O. Serhadhi and M.L. Ziegler, *J. Organomet. Chem., 347* (1988) 237.
16 W.A. Herrmann, J. Rohrmann, M.L. Ziegler and T. Zahn, *J. Organomet. Chem., 273* (1984) 232.
17 G.J. Kubas, H.J. Wasserman and R. Ryan, *Organometallics, 4* (1985) 419.
18 C. Hecht, E. Herdtweck, J. Rohrmann, W.A. Herrmann, W. Beck and P.M. Fritz, *J. Organomet. Chem., 330* (1987) 389.
19 E. Rottinger, V. Kullmer and H. Vahrenkamp, *J. Organomet. Chem., 150* (1978) C6.
20 (a) W.-D. Stohrer and R. Hoffmann, *J. Am. Chem. Soc., 94* (1972) 779; (b) Y. Jean, A. Lledos, J.K. Burdett and R. Hoffmann, *J. Am. Chem. Soc., 110* (1988) 4506; (c) Y. Jean, A. Lledos, J.K. Burdett and R. Hoffmann, *J. Chem. Soc., Chem. Commun.,* (1988) 140.
21 (a) G. Parkin, *Chem. Rev., 93* (1993) 887; (b) K. Yoon, G. Parkin and A.L. Rheingold, *J. Am. Chem. Soc., 114* (1992) 2210; (c) J. Song and M.B. Hall, *Inorg. Chem., 30* (1991) 4433.
22 E.D. Jemmis and A.C. Reddy, *J. Am. Chem. Soc., 112* (1990) 722.
23 (a) V.C. Gibson and M. McPartlin, *J. Chem. Soc., Dalton Trans.,* (1992) 947; (b) J.M. Mayer, *Angew. Chem., Int. Ed. Engl., 31* (1992) 286; (c) G. Parkin, *Acc. Chem. Res., 25* (1992) 455.
24 C. Mealli and L. Sacconi, *Inorg. Chem., 21* (1982) 2870.
25 Z. Lin and M.B. Hall, *Inorg. Chem., 30* (1991) 3817.
26 N.M. Kostic and R.F. Fenske, *J. Organomet. Chem., 233* (1982) 337.
27 H. Fujimoto and R. Hoffmann, *J. Phys. Chem., 78* (1974) 1167.
28 (a) R. Hoffmann, *J. Chem. Phys., 39* (1963) 1397; (b) R. Hoffmann and W.N. Lipscomb, *J. Chem. Phys., 36* (1962) 2179.
29 W.J. Hehre, L. Radom, P.v.R. Schleyer and J.A. Pople, *Ab initio Molecular Orbital Theory*, Wiley, New York, 1986.
30 P.J. Hay and W.R. Wadt, *J. Chem. Phys., 82* (1985) 270, 284, 289.
31 B.E.R. Schilling, R. Hoffmann and D.L. Lichtenberger, *J. Am. Chem. Soc., 101* (1979) 585.
32 E.D. Jemmis, A.R. Pinhas and R. Hoffmann, *J. Am. Chem. Soc., 102* (1980) 2576.
33 R. Hoffmann, H. Fujimoto, J.R. Swenson and C.C. Wan, *J. Am. Chem. Soc., 95* (1973) 7644.
34 (a) A. Vela, J.L. Gazquez. *J. Phys. Chem., 92* (1988) 5688; (b) R.H. Summerville and R. Hoffmann, *J. Am. Chem. Soc., 98* (1976) 7240; (c) D.M. Hoffmann, R. Hoffmann and C.R. Fiesel, *J. Am. Chem. Soc., 104* (1982) 3858; (d) A. Dedieu, T.A. Albright and R. Hoffmann, *J. Am. Chem. Soc., 101* (1979) 3141.

Appendix

The atomic parameters used in extended Hückel calculations are taken from earlier works [28,34]. The bond distances and bond angles from diffraction studies are used wherever available. For the hypothetical compounds the bond distances are taken from X-ray structures of related complexes. The bond distances which are used are given below. The distances C–O, C–C (Cp ring) and C–H are kept at 1.17, 1.40 and 1.08 Å in all calculations. The geometry employed around the metal is different in the linear and in the triangular forms, but similar in the linear and bent forms. When we go from the linear to the triangular forms, the changes in the geometry are as follows: E–M–Cp angle changed from 127° to 117°. M–M–C (of CO) angles are

90° and 90° in linear geometry and 78° and 110° in triangular geometry. CO–M–CO angle is varied from 90° to 80°. The M–E distance is kept constant during the change. The two Cp rings are *trans* to each other, hence the maximum symmetry possible is C_2. A higher symmetry is not allowed because the C_{2v} geometry suffers from steric interactions in the triangular form.

	W	Re	Cr	Mn
M–S	2.324	2.381	2.073	2.100
M–Se	2.480	2.493	2.210	2.356
M–Te	2.670	2.679	2.420	2.460
M–Cp	2.000	1.963	1.846	1.838
M–C	2.000	1.936	1.866	1.810