Theoretical investigation of triple bond in molybdenum complexes *trans*-[X(PMe₃)₄ Mo≡E(Mes)] (X = F, Cl, Br, I; E = Si, Ge, Sn, Pb): A DFT study

Krishna K. Pandey *, Pankaj Patidar

School of Chemical Sciences, Devi Ahilya University Indore, Khandwa Road, Indore 452001, India

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ABSTRACT

Quantum-chemical calculations were used to investigate the molecular and electronic structures as well as bonding energies of the molybdenum–ylidyne complexes *trans*-[X(PMe₃)₄Mo≡E(Mes)] (X = F, Cl, Br, I; E = Si, Ge, Sn, Pb) at the BP86/TZ2P/ZORA level of theory. The calculated geometrical results are in excellent agreement with the available experimental results. The Mo≡E bond distances are significantly short, and the calculated Pauling Mo–E bond orders are $\sim$2.40–2.65. The electronic structures of the Mo≡E bonds show the presence of genuine triple bond containing an σ-bond and two π-bonds in all studied complexes. The Mo≡E σ-bonds are polarized towards the heavier group 14 elements while the π-bonds are polarized towards the molybdenum metal. The partial charges on the [EMes]⁺ fragments (0.67–0.93) indicate that the overall charges flow from the metal fragments to the [EMes]⁺ fragments. The nature of Mo≡E bonds also investigated by means of energy decomposition analysis which reveals that the metal–ligand π-orbital interactions between [X(PMe₃)₄Mo]⁻ and [EMes]⁺ fragments are the most dominant interactions, contributing (80–85%) to the total ΔE_{orb} terms. The strength of Mo≡E bonds mainly depends on the π-acceptor ability of [EMes]⁺ group. It decreases when 14 group element becomes heavier in the trend Si > Ge > Sn > Pb and in the order F > Cl > Br > I.

1. Introduction

The coordination chemistry of transition metal–carbyne complexes has developed rapidly after the synthesis of first transition metal–carbyne complex in 1973 [1]. These complexes are pivotal subject of the experimental and theoretical research in past four decades because of their great utilities in organometallic catalytic processes and organic synthesis [1–17]. In comparison, the chemistry of heavier analogues of carbyne ligand ER (E = Si, Ge, Sn, Pb) is relatively less developed and only few complexes featuring metal–silicon, metal–germanium, metal–tin or metal–lead triple bonds have been obtained so far [18,19].

The first transitional metal germylyne complex [(η⁵-C₅H₅)(CO)₂Mo≡GeR] (R = C₆H₃-2,6-Trip₂), which was first compound featuring a triple bond to a heavier group 14 elements also, was isolated by Simons and Power in 1996 [20]. Afterwards, a series of the germylyne complexes of chromium and tungsten [(η⁵-C₅H₅)(CO)₂M≡GeR] (M = Cr, Mo, W; R = C₆H₃-2,6-Mes₂, C₆H₃-2,6-Trip₂) has also been reported [21]. This chemistry of triply bonded compounds becomes more interesting when another class of germylidyne complexes *trans*-[X(dppe)₂M≡Ge(η¹-Cp*)] (X = Cl, Br, I; M = Mo, W) was isolated and characterized by Filippou et al. [22,23]. Later, his

group reported numerous octahedral complexes of germylidyne, stannylidyne and plumbylidyne ligands [24–31]. The spectral study of some stannylidyne complexes has also been performed by mean of Mössbauer spectroscopy [32]. However, only single example of true, neutral transition metal–silylidyne complex [(η⁵-C₅H₅)(CO)₂M≡Si-C₆H₃-2,6-Trip₂] is known so far [33,34]. A cationic molybdenum complex with considerable silylidyne character, [(η⁵-C₅Me₅)(dmpe)(H)Mo≡SiMes][B(C₆F₅)₄] (dmpe = Me₂PCH₂CH₂PMe₂) [35] and a base-stabilized complex [(η⁵-C₅Me₅)(PMe₃)₂Ru{Si(SC₆H₄-4-Me)(bipy)}](OTf)₂ [36] containing a singly-bonded silylidyne ligand have also been described in literature. All structurally characterized transition metal–ylidyne complexes and their important structural parameters are summarized in Chart 1.

The theoretical calculations on metal–ylidyne complexes, in comparison to carbyne complexes, are rather scarce. Only few quantum chemical calculations to investigate the structural and bonding aspects of transition metal–silylidyne, germylidyne, stannylidyne and plumbylidyne complexes have been carried out previously [37–41]. Frenking and coworkers presented bonding patterns of W≡E bonds in [Cl(CO)₄W≡EH] and [Cl₃W≡EH] (E = C, Si, Ge, Sn, Pb) complexes [38] while we differentiate the bonding and electronic structures of linear metal ylidyne complexes and bent metallo-ylidene complexes of chromium, molybdenum and tungsten [39,40]. Recently, bonding energy analysis of M≡E bonds in octahedral cationic complexes *trans*-[(MeCN)(PMe₃)₄M≡EMes]⁺ (M = Mo, W; E = Si, Ge, Sn, Pb) has also been reported [41].

* Corresponding author. Tel.: +91 731 2460208; fax: +91 731 2762342.
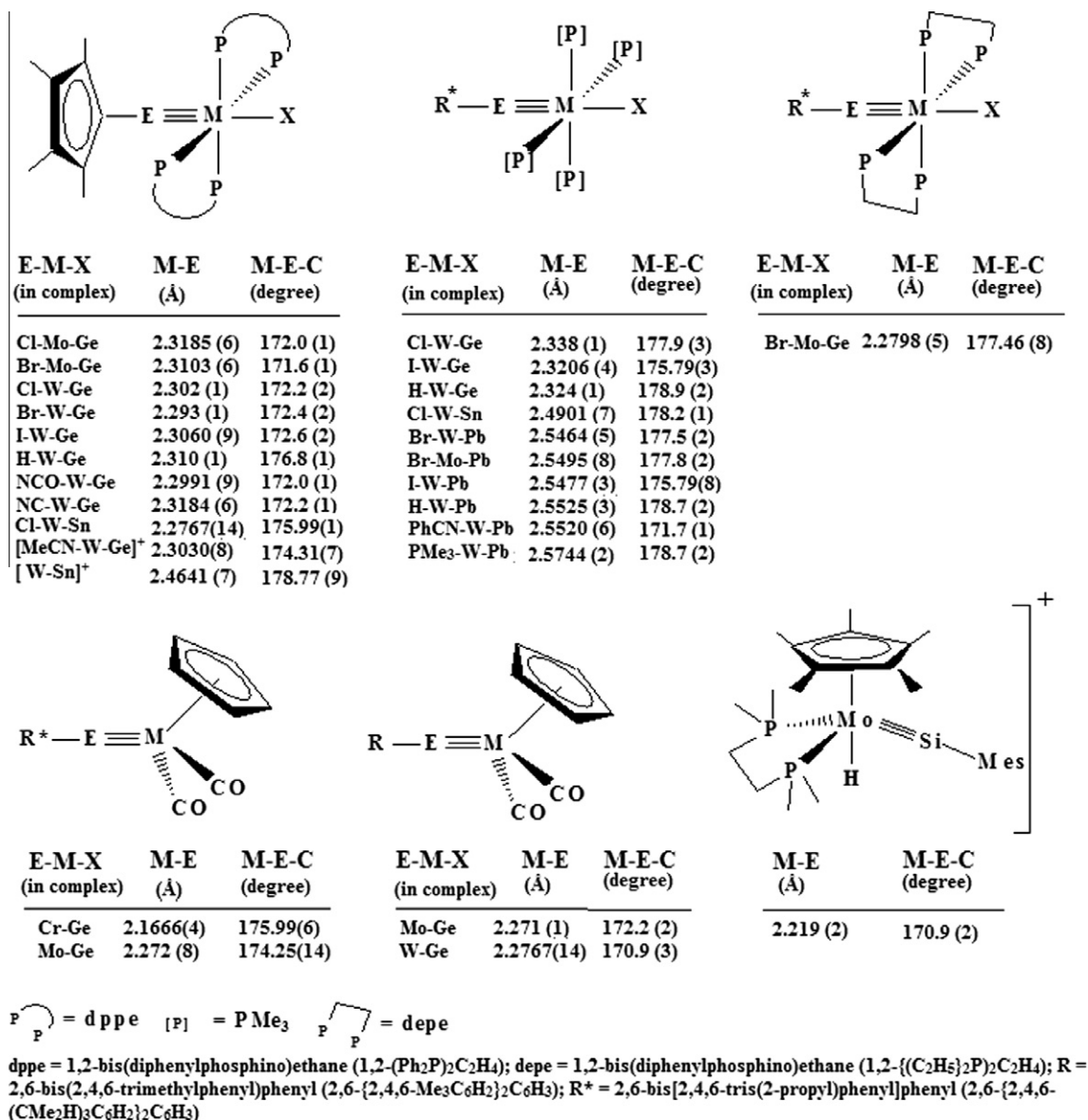*E-mail address:* kkpandey.schem@dauniv.ac.in (K.K. Pandey).

E-M-X (in complex)	M-E (Å)	M-E-C (degree)
Cl-Mo-Ge	2.3185 (6)	172.0 (1)
Br-Mo-Ge	2.3103 (6)	171.6 (1)
Cl-W-Ge	2.302 (1)	172.2 (2)
Br-W-Ge	2.293 (1)	172.4 (2)
I-W-Ge	2.3060 (9)	172.6 (2)
H-W-Ge	2.310 (1)	176.8 (1)
NCO-W-Ge	2.2991 (9)	172.0 (1)
NC-W-Ge	2.3184 (6)	172.2 (1)
Cl-W-Sn	2.2767(14)	175.99(1)
[MeCN-W-Ge]+	2.3030(8)	174.31(7)
[W-Sn]+	2.4641 (7)	178.77 (9)

E-M-X (in complex)	M-E (Å)	M-E-C (degree)
Cl-W-Ge	2.338 (1)	177.9 (3)
I-W-Ge	2.3206 (4)	175.79(3)
H-W-Ge	2.324 (1)	178.9 (2)
Cl-W-Sn	2.4901 (7)	178.2 (1)
Br-W-Pb	2.5464 (5)	177.5 (2)
Br-Mo-Pb	2.5495 (8)	177.8 (2)
I-W-Pb	2.5477 (3)	175.79(8)
H-W-Pb	2.5525 (3)	178.7 (2)
PhCN-W-Pb	2.5520 (6)	171.7 (1)
PMe3-W-Pb	2.5744 (2)	178.7 (2)

E-M-X (in complex)	M-E (Å)	M-E-C (degree)
Br-Mo-Ge	2.2798 (5)	177.46 (8)

E-M-X (in complex)	M-E (Å)	M-E-C (degree)
Cr-Ge	2.1666(4)	175.99(6)
Mo-Ge	2.272 (8)	174.25(14)

E-M-X (in complex)	M-E (Å)	M-E-C (degree)
Mo-Ge	2.271 (1)	172.2 (2)
W-Ge	2.2767(14)	170.9 (3)

M-E (Å)	M-E-C (degree)
2.219 (2)	170.9 (2)

dppe = 1,2-bis(diphenylphosphino)ethane (1,2-(Ph2P)2C2H4); depe = 1,2-bis(diphenylphosphino)ethane (1,2-{(C2H5)2P}2C2H4); R = 2,6-bis(2,4,6-trimethylphenyl)phenyl (2,6-{2,4,6-Me3C6H2}2C6H3); R* = 2,6-bis[2,4,6-tris(2-propyl)phenyl]phenyl (2,6-{2,4,6-(CMe2H)3C6H2}2C6H3)

Chart 1. An overview of experimentally known transition metal–ylidyne complexes.

Here we set out to explore the chemistry of transition metal–ylidyne complexes and report a detailed theoretical study of several molybdenum–ylidyne complexes trans-[X(PMe3)4Mo≡E(Mes)] (**I**, E = Si, X = F; **II**, E = Ge, X = F; **III**, E = Sn, X = F; **IV**, E = Pb, X = F; **V**, E = Si, X = Cl; **VI**, E = Ge, X = Cl; **VII**, E = Sn, X = Cl; **VIII**, E = Pb, X = Cl; **IX**, E = Si, X = Br; **X**, E = Ge, X = Br; **XI**, E = Sn, X = Br; **XII**, E = Pb, X = Br; **XIII**, E = Si, X = I; **XIV**, E = Ge, X = I; **XV**, E = Sn, X = I; **XVI**, E = Pb, X = I) with linear X–Mo–E and Mo–E–C bonding. To best of our knowledge, only trans-[Br(PMe3)4Mo≡Pb-C6H3-2,6-Trip2] complex among the complexes under study was theoretically investigated so far [29]. The bulky organic substituent at group 14 atoms is replaced by mesityl group (Mes = 2,4,6-Me3C6H2). The model consider a formally positively charged ligand [EMes]+, which serves as two-electron σ-donor and four electron π-accepter and bonding can be described with DCD (Dewar–Chatt–Ducanson) model [42,43]. The π-interactions in the all optimized molecules with C$_s$ symmetry are labeled then as in-plane ($\pi_\parallel$) and out-of-plane ($\pi_\perp$) π contributions as shown in Fig. 1. A characteristic feature of these complexes is X–M–ER linkages, are very close to linearity.

In the current work we would like to present (i) the molecular and electronic structure of the molybdenum–ylidyne complexes trans-[X(PMe3)4Mo≡E(Mes)] (X = F, Cl, Br, I; E = Si, Ge, Sn, Pb), (ii) the binding energies as well as extent of σ and π characters of the Mo≡E bonds and (iii) the relative strength of covalent and electrostatic interactions. Apart from this we are also interested in the structural trans effect of the ligand X on the Mo≡E bonds. In order to address the above features we have calculated the geometries, electronic structures and bond dissociation energies of four sets of complexes (**I–XVI**) using density functional theory (BP86/TZ2P). The bonding situation in the molecules was investigated with the help of energy decomposition analysis (EDA) that makes it possible to quantitatively estimate the contributions of orbitals which possess different symmetry to the overall metal–ligand orbital interactions. A short description of the methods is given in the following section.

2. Computational method

The geometries of all complexes trans-[X(PMe3)4Mo≡E(Mes)] (X = F, Cl, Br, I; E = Si, Ge, Sn, Pb) (**I–XVI**) have been optimized at the gradient corrected DFT level of theory using the exchange