#### FULL PAPER



## CHEMISTRY WILEY

# Quadruple chemical bonding in the diatomic anions TcN<sup>-</sup>, RuC<sup>-</sup>, RhB<sup>-</sup>, and PdBe<sup>-</sup>

#### Demeter Tzeli<sup>1,2</sup>

<sup>1</sup>Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Athens, Greece

<sup>2</sup>Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece

#### Correspondence

Demeter Tzeli, Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, Athens 157 84, Greece. Email: tzeli@chem.uoa.gr

#### **Funding information**

National and Kapodistrian University of Athens, Special Accounts for Research Grants, Grant/Award Number: SONFM:17034

#### Abstract

Quadruple bonding is uncommon for main group elements and the identification of species forming such bonds is remarkably interesting particularly in diatomic anions for which there is a lack of information. Here, it is found that the MX<sup>-</sup> anions, TcN<sup>-</sup>, RuC<sup>-</sup>, RhB<sup>-</sup>, and PdBe<sup>-</sup>, present quadruple bonding, as do the corresponding MX neutrals, even though a different type of  $\sigma^2$  bond is involved in  $\Sigma^+$  states of neutral and anions. Specifically, the ground states ( $X^2\Delta$  or  $X^2\Sigma^+$ ) of the four anions and their first excited states ( $A^2\Sigma^+$  or  $A^2\Delta$ ) of TcN<sup>-</sup>, RuC<sup>-</sup>, and RhB<sup>-</sup> present quadruple bonds consisting of two  $\sigma$  and two  $\pi$  bonds:  $(4d_{z2} - 2p_z)^2$ ,  $5p_z^0 \leftarrow 2s^2$ ,  $(4d_{xz} - 2p_x)^2$ , and  $(4d_{yz} - 2p_y)^2$ . Bond lengths, dissociation energies, spectroscopic data and electron affinities were calculated via high-level multireference and coupled-cluster methodology using the aug-cc-pV5Z<sub>x</sub>(-PP)<sub>M</sub> basis set. Strong bonding results in short bond lengths ranging from 1.602 (TcN<sup>-</sup>) to 1.944 (PdBe<sup>-</sup>) Å. Adiabatic (diabatic) binding energies reach up to 139 (184) kcal/mol. Electron affinities (EA) were calculated at 1.368 (TcN), 1.242 (RuC), 0.873 (RhB), 0.743 (PdBe) eV. Only for RhB has EA been measured experimentally at 0.961 eV, in good agreement with the value reported here.

#### KEYWORDS

coupled cluster calculations, multireference calculations, PdBe<sup>-</sup>, quadruple bonding, RhB<sup>-</sup>, RuC<sup>-</sup>, TcN<sup>-</sup>

#### 1 | INTRODUCTION

Quadruple bonding is very rare for main group elements and recognizing species forming such bonds can advance both the basic interpretation of bonding of diatomic species and the examination of other potential species forming such bonds. Additionally, the identification of a quadruple bond motif is remarkably interesting, particularly in diatomic anions of transition metals where there is a surprising lack of information in the literature. Furthermore, there is one measured experimental electron affinity (EA) for only one of the four calculated species which is in good agreement with the calculated EA; for the remaining species, this study will provide experimentalists with useful data for future studies.

Transition metals have very interesting properties which result from their partially occupied d orbitals with loosely bound electrons. These metals

are very hard and malleable; they have high melting and boiling points, high electrical and thermal conductivity; they form colored compounds due to d-d electronic transitions. They often exhibit high catalytic activity and tend to form paramagnetic compounds because of the unpaired d electrons <sup>[1]</sup>. These properties are consequences of the nature of their chemical bonding, hence their study is a very active area of research <sup>[2–8]</sup>.

The analysis of the chemical bonding is a very fundamental aspect of chemistry. The study of quadruple bonding in diatomic species involving main group elements attracts researchers' interest. For instance, the exact multiplicity of the bond of the C<sub>2</sub> molecule was carefully examined and analyzed by many theoretical groups <sup>[9]</sup>. Furthermore, chemical bonding in diatomic anions in particular has not received the attention it deserves. This study is trying to fill this gap by looking at the formation of quadruple bonds in diatomic anions.

In 2020, two studies were published on the quadruple bonding of 2nd row transition metals with main group elements <sup>[10,11]</sup> and one study on the nature of the bonding of 3rd row transition metals <sup>[12]</sup>. The quadruple bonding in the ground state of RhB was first reported by Cheung et al. <sup>[10]</sup>, while our group <sup>[11]</sup> found that four molecules, i.e., TcN, RuC, RhB and PdBe (MX), present ground states with a quadruple bond and in the case of TcN, RuC, and RhB, their two lowest excited states also have guadruple bonds. The necessary requirements for the occurrence of quadruple bonds were determined, i.e., (i) the existence of low-lying atomic states that have low lying unoccupied orbitals that can receive electrons via dative bonds and (ii) atoms with doubly occupied orbitals that can form dative bonds. Here we examine if electron attachment destroys or preserves quadruple bonding. Interestingly enough, we concluded that quadruple bonding is found in the anions, but it involves different orbitals than in the neutrals in the  $\Sigma^+$  states, see below.

It should be noted that while there are experimental and theoretical data on the neutral TcN <sup>[11,13,14],</sup> RuC <sup>[11,13,15-18],</sup> RhB <sup>[10,11,13,19]</sup> and PdBe <sup>[11]</sup> molecules, the literature on the corresponding anions is very limited, see below. A synopsis of all previous studies on the four neutral MX species is reported in ref. [11]. Regarding the MX<sup>-</sup> anions, there are only three studies on two anions, i.e., on the <sup>2</sup>Σ<sup>+</sup> state of RuC<sup>-</sup> <sup>[13,15]</sup> and RhB<sup>-</sup> <sup>[10,13]</sup>. For RuC<sup>-</sup> a state of <sup>2</sup>Σ<sup>+</sup> symmetry was calculated via the DFT methodology <sup>[13,15]</sup> as its ground state, while in the present work, the <sup>2</sup>Σ<sup>+</sup> state was calculated as the first excited state and the <sup>2</sup>Δ state found as the ground one. For RhB<sup>-</sup>, DFT <sup>[10,15]</sup> and CCSD(T) <sup>[10]</sup> data are provided for its  $X^2\Sigma^+$  ground state. Cheung et al. <sup>[10],</sup> reported that a quadruple bonding is formed in the  $X^2\Sigma^+$  state of RhB<sup>-</sup> and they measured via photoelectron spectroscopy its electron affinity (EA) at 0.961 eV <sup>[10]</sup>. Finally, there is nothing in the literature on the TcN<sup>-</sup> and PdBe<sup>-</sup> anions.

The aims of the present paper are: i) to present diatomic negatively charged species forming quadruple bonding with main group elements ii) to provide spectroscopic data, which are missing from the literature, on the two lowest states of the four anions,  $MX^-$ , i.e., TcN<sup>-</sup>, RuC<sup>-</sup>, RhB<sup>-</sup>, and PdBe<sup>-</sup> via high-level multi reference configuration interaction (MRCISD) and coupled cluster (RCCSD(T)) theoretical calculations; iii) to calculate their EA; iv) to analyze the bonding; and v) to study how the attachment of an electron affects the spectroscopic data of MX.

#### 2 | COMPUTATIONAL DETAILS

The MX<sup>-</sup> anions were studied by employing the correlation consistent basis sets of Dunning et al. <sup>[20]</sup> aug-cc-pV5Z, (15s, 9p, 5d, 4f, 3g, 2h)  $\rightarrow$  [7s, 6p, 5d, 4f, 3g, 2h] for X, X = Be-N and of Peterson et al. <sup>[21]</sup> aug-cc-pV5Z-PP, (17s, 14p, 12d, 5f, 4g, 3h, 2i)  $\rightarrow$  [8s, 8p, 7d, 5f, 4g, 3h, 2i] for M, M = Tc-Pd. The latter ones employ accurate core relativistic pseudo-potentials for the  $1s^22s^22p^63s^23p^6$  electrons and treat the  $4s^24p^6(5s4d)$  <sup>[7-10]</sup> electrons of the transition metals in the ab initio calculation. The multireference configuration interaction + single + double excitations (MRCISD) <sup>[22],</sup> MRCISD+Q <sup>[23]</sup> where the Davidson correction (+Q) was included in MRCISD, and restricted

coupled cluster + singles + doubles + perturbative triples (RCCSD(T)) <sup>[24]</sup> methodology was applied.

At first, complete active space self-consistent field (CASSCF) calculations were carried out, where the 13 "valence" electrons were allotted to 10 valence orbitals, i.e., six (5s4d) of  $M^{-,0}$  + four (2s2p) orbitals of X<sup>-,0</sup>, followed by the MRCISD calculations <sup>[22]</sup>. The size of the MRCISD spaces is about  $9 \times 10^8$  and it is reduced to about  $4 \times 10^6$  CSFs after applying the internal contraction approximation (icMRCISD)<sup>[22]</sup>. At the RCCSD(T) level of calculations, the 2s2p electrons of  $X^{-,0}$  and the 4d5s electrons of  $M^{-,0}$  were correlated; the RCCSD(T) spaces consists of  $1.5 \times 10^6$  CSFs. In order to evaluate our RCCSD(T), which is a single-reference method, the single  $(t_1)$  and the double  $(t_2)$  amplitudes and the  $T_1$  diagnostic are checked. It is found that in all calculations the  $t_1$  and  $t_2$  amplitudes were very small. In most cases, they are smaller than 0.05. Moreover, the  $T_1$  diagnostic is about 0.06 or less in all calculations. These small values of  $t_1$  and  $t_2$ amplitudes and  $T_1$  diagnostic indicate that the single reference RCCSD(T) method is appropriate for the calculated states of the species. All calculations were done under C<sub>2v</sub> symmetry constraints, however the CASSCF wave functions possess correct angular momentum symmetry, i.e.,  $|\Lambda| = 0$  ( $\Sigma^+$ ) and 2 ( $\Delta$ ), i.e.,  $\Delta$  is a linear combination of  $A_1$  and  $A_2$  symmetries, whereas  $\Sigma^+$  corresponds to  $A_1$  symmetry. Of course, MRCISD and RCCSD(T) wavefunctions do not display in general pure spatial angular momentum symmetry, but A<sub>1</sub> for  $\Sigma^+$  and A<sub>1</sub> or  $A_2$  for  $\Delta$  states. For all MX<sup>-</sup> anions the main configuration state functions are:

$$\begin{split} & \left|{}^{2}\Delta\right\rangle_{A_{1}+A_{2}} \cong 0.9 \left|{}^{1}\!\!\sqrt{_{2}} \Big(1\sigma^{2}2\sigma^{2}3\sigma^{2}1\pi_{x}^{2}1\pi_{y}^{2}\Big) \big(1\delta_{+}^{1}1\delta_{-}^{2}+1\delta_{+}^{2}1\delta_{-}^{1}\big) \right. \text{ and } \\ & \left|{}^{2}\sum^{+}\right\rangle \cong 0.9 \big|1\sigma^{2}2\sigma^{2}3\sigma^{1}1\pi_{x}^{2}1\pi_{y}^{2}1\delta_{+}^{2}1\delta_{-}^{2}\Big\rangle. \end{split}$$

Potential energy curves (PEC) up to R = 15 Å have been plotted at the MRCISD and MRCISD+Q levels of theory for all anions and additional at RCCSD(T) for PdBe<sup>-</sup>. The electron affinities (EA), bond distances, dissociation energies (D<sub>e</sub>; adiabatic D<sub>e</sub><sup>a</sup> and diabatic D<sub>e</sub><sup>d</sup>), relative energy ordering (T<sub>e</sub>), and other spectroscopic constants are computed at all used levels of theory, i.e., MRCISD, MRCISD+Q, and RCCSD(T). It should be noted that spin-orbit effects are not considered here given that accurate core relativistic pseudo-potentials are employed and only 15–18 electrons of the transition metal atoms are treated in the ab initio calculations.

Finally, the bonding of the states is analyzed; it is depicted pictorially via a valence bond Lewis (vbL) diagram <sup>[25]</sup> and via 3D contour plots of the valence molecular orbitals. Note, that the bond order is the number of chemical bonds between the atoms, i.e., a whole bond corresponds to a pair of electrons, while a half bond corresponds to a bond with one electron. Both Mulliken and NBO population analyses have been carried out, however while they confirm the bonding, there are differences between the two analyses for the total charge of metal; namely the Mulliken analysis indicates more negative charge on the metal than NBO, see Table S5. However, the differences of both analyses between the neutral MX and the MX<sup>-</sup> are the same, showing clearly where the extra electron is located. All CASSCF, MRCISD, and RCCSD(T) calculations were carried out with the MOLPRO <sup>[26]</sup> suite of codes. 1128 WILEY- CHEMISTRY

#### 3 | RESULTS AND DISCUSSION

The energy separation of the atomic states involved in the MX<sup>-</sup> anions are presented in Tables 1 and S1. Bond distances, dissociation energies, harmonic frequencies, and anharmonic corrections, rotational vibrational couplings, centrifugal distortions and relative energy differences of the isoelectronic TcN<sup>-</sup>, RuC<sup>-</sup>, RhB<sup>-</sup>, and PdBe<sup>-</sup> anions at various levels of theory are given in Tables 2 and S3. Data regarding the main CSFs are reported in Table S2. The electron affinities of the diatomic species and the involved atoms are presented in Tables 3 and S6. The RCCSD(T) EAs are in better agreement with the experimental ones for the transition metals than the EAs values obtained via MR methodologies. Thus, our RCCSD(T) EA are reported below. The largest deviation between experiment and theory is observed for Tc at 0.24 eV and the least one for Ru at 0.08 eV. Regarding the energetics both MRCISD+Q and RCCSD(T) predict similar data, while regarding bond distances all three methodologies yield the same results.

#### 3.1 | MX<sup>-</sup>

#### 3.1.1 | TcN<sup>-</sup>

There are no previous theoretical or experimental studies on TcN<sup>-</sup>. Both  $X^2\Delta$  and  $A^2\Sigma^+$  correlate to the ground state products Tc<sup>-(5</sup>D;  $4d^{6}5s^{2}$ ) + N(<sup>4</sup>S; 2s<sup>2</sup>2p<sup>3</sup>) and present an avoided crossing around 3.5 Å with excited  $^{2}\Delta$  and  $^{2}\Sigma^{+}$  states which correlate to Tc<sup>-(5</sup>F; 4d<sup>7</sup>5s<sup>1</sup>) + N (<sup>4</sup>S), see Figure 1. The  $X^2\Delta$  presents a second avoided crossing with an excited  $^{2}\Delta$  state at 2.3 Å, and obtains the character of the ground state products, i.e.,  $Tc^{-(^{5}D)} + N(^{4}S)$ . Both states present quadruple bonding, i.e., two  $\sigma$  and two  $\pi$  bonds,  $1\sigma^2 2\sigma^2 \ 1\pi^2 2\pi^2$  i.e.,  $5p_z^0 \leftarrow 2s^2$ ,  $(4d_{z2}^{\uparrow}-2p_{z}^{\downarrow})^{2}$ ,  $(4d_{xz}^{\uparrow}-2p_{x}^{\downarrow})^{2}$ ,  $(4d_{yz}^{\uparrow}-2p_{y}^{\downarrow})^{2}$ , which is depicted in Scheme 1, and given in Table S7. Note that a  $5s5p_{7}4d_{72}$  hybridization is observed at the  $\sigma$  bonds; the molecular orbitals are plotted in Figure S14. The formation of the  $5p_z^0 \leftarrow 2s^2$  bond is supporting also by the calculated charge on the 5p<sub>7</sub> orbital via Mulliken and NBO analysis. Comparing neutral and anion species, while guadruple bonding is observed in both TcN<sup>-</sup>( $X^2\Delta$  and  $A^2\Sigma^+$ ) and TcN( $X^3\Delta$ ,  $^1\Delta$  and  $^1\Sigma^+$ ), only in  $\Delta$  states the bonding type is the same for both neutral and anion. In the  $\Sigma^+$  states, the type of  $2\sigma^2$  bond changes from  $5s^0 \leftarrow 2s^2$  in  ${}^{1}\Sigma^{+}(MX)$  to  $5p_{z}{}^{0} \leftarrow 2s^{2}$  in  ${}^{2}\Sigma^{+}(MX^{-})$  because the attached electron is located at the empty 5s orbital of the Tc of  $\Sigma^+$  and as a result the 5p<sub>z</sub> is preferred for the dative bond. In  $\Delta$  states, the attached electron is located at the semi-occupied 5s and the quadruple character of the bonding does not change because the 5s orbital is not mainly involved in the bonding.

The bond lengths of the X<sup>2</sup> $\Delta$  and A<sup>2</sup> $\Sigma$ <sup>+</sup> states are 1.609 (1.610) and 1.602 (1.607) Å, respectively, at the MRCI+Q (RCCSD(T)) level of theory. The binding energies of the two states with respect to their correlated products are 130.9 (134.6) and 109.9 (112.4) kcal/mol, respectively, see Table 2. For the A<sup>2</sup> $\Sigma$ <sup>+</sup> state the binding energy with respect to its in situ, i.e., diabatic products is 152.4 (153.2) kcal/mol.

Comparing the anions with the neutral species, the bond lengths of the  $X^2\Delta$  and  $A^2\Sigma^+$  states of TcN<sup>-</sup> are elongated by about 0.01 Å compared to  $X^{3}\Delta(^{1}\Delta)$  and  $^{1}\Sigma^{+}$  states of TcN <sup>[11];</sup> note that the only difference between the two  $\Delta$  states of TcN is the spin multiplicity, i.e.,  $\uparrow\uparrow(X^3\Delta)$  and  $\uparrow\downarrow(^1\Delta)$ . The small elongation of bond distance is attributed to the attachment of an electron to a non-bonding orbital. Regarding the binding energy with respect to the correlated [ground state] atomic products are: 123.3 [111.6]<sup>11</sup> kcal/mol for  $X^3\Delta$  and 131.4 [96.4]<sup>11</sup> kcal/mol for  $^{1}\Delta$  of TcN compared to 130.9 kcal/mol of  $X^{2}\Delta$  kcal/mol at the MRCISD+Q level of theory, showing that the electron attachment further stabilizes the  $\Delta$  states by about 10 [20] kcal/mole, respectively. On the contrary, for the  $\Sigma^+$  states, the binding energy with respect to diabatic (adiabatic) [ground state] products are: 160.1 (150.8)  $[97.1]^{11}$  kcal/mol for  ${}^{1}\Sigma^{+}$ (TcN)  ${}^{[11]}$ , while for the anion is 152.4 (109.9) [109.9] kcal/mol  $A^2\Sigma^+(TcN^-)$  at the MRCISD+Q level of theory; i.e., the electron attachment further destabilizes the  $\Sigma^+$  state with respect to adiabatic products, but it stabilizes it by 10 kcal/mol with respect to the ground state products.

The potential energy curves of TcN<sup>-</sup> and TcN are depicted in Figures 2 and S1–S3. The X<sup>2</sup> $\Delta$  and A<sup>2</sup> $\Sigma$ <sup>+</sup> states of TcN<sup>-</sup> are close lying to the five lowest states of TcN, i.e., X<sup>3</sup> $\Delta$ , <sup>1</sup> $\Sigma$ <sup>+</sup>, <sup>1</sup> $\Delta$ , <sup>3</sup> $\Sigma$ <sup>-</sup> and <sup>5</sup>II. The EA of Tc was calculated at 0.310 eV, while experimentally it was measured at 0.55 (20) eV <sup>[30]</sup>. The EA of TcN was calculated at 1.368 eV, showing that the bonding stabilizes the electron attachment significantly.

#### 3.1.2 | RuC<sup>-</sup>

The EA of the C and Ru atoms are 1.238 and 1.127 eV, in excellent agreement with the experimental values of 1.2621 <sup>[29]</sup> and 1.0464 <sup>[31]</sup> eV. As a result the  $X^2\Delta$  and  $A^2\Sigma^+$  states of RuC<sup>-</sup> correlate to Ru(a<sup>5</sup>F; 4d<sup>7</sup>5s<sup>1</sup>) + C<sup>-</sup>(<sup>4</sup>S; 2s<sup>2</sup>2p<sup>3</sup>). However, both states present

**TABLE 1** Energy separation (eV) of atomic states of M<sup>-</sup> (M = Tc, Ru, Rh, and Pd) and of C<sup>-</sup> anions at MRCISD, MRCISD+Q, and RCCSD(T)/ aug-cc-pV5Z(-PP)M

Method <sup>a</sup>	$\begin{array}{l} Tc^{-}  ({}^{5}F \leftarrow {}^{5}D) \\ 4d^{7}5s^{1} \leftarrow 4d^{6}5s^{2} \end{array}$	$\begin{array}{l} Ru^{-}(b^{4}F \leftarrow a^{4}F) \\ 4d^{8}5s^{1} \leftarrow 4d^{7}5s^{2} \end{array}$	$\begin{array}{l} Rh^{-}(a^{3}D \leftarrow a^{3}F) \\ 4d^{9}5s^{1} \leftarrow 4d^{8}5s^{2} \end{array}$	Pd <sup>–</sup> (a²D ← a²S) 4d°5s² ← 4d <sup>10</sup> 5s <sup>1</sup>	$\begin{array}{l} C^{-}(a\ ^{2}D \leftarrow a^{4}S) \\ 2s^{2}2p^{3} \leftarrow 2s^{2}2p^{3} \end{array}$
MRCISD	1.773	1.508	1.155	0.332	1.490
MRCISD+Q	1.735	1.555	0.693	0.279	1.349
RCCSD(T)	1.769	1.365	0.697	0.357	1.463

<sup>a</sup>Internally contracted MRCI; Q refers to the Davidson correction.

**TABLE 2** Bond lengths  $r_e$  (Å), binding energies  $D_e$  (kcal/mol), harmonic frequencies and anharmonic corrections  $\omega_e$ ,  $\omega_e x_e$  (cm<sup>-1</sup>), rotational vibrational couplings  $\alpha_e$  (cm<sup>-1</sup>), centrifugal distortions  $\overline{D}_e$  (cm<sup>-1</sup>), and energy differences  $T_e$  (kcal/mol) of the TcN<sup>-</sup>, RuC<sup>-</sup>, RhB<sup>-</sup>, and PdBe<sup>-</sup> anions at MRCISD, MRCISD+Q, and RCCSD(T)/aug-cc-pV5Z(-PP)<sub>M</sub>

State	Methods <sup>a</sup>	r <sub>e</sub>	D <sub>e</sub> <sup>a</sup> (D <sub>e</sub> <sup>d</sup> ) <sup>b</sup>	ω <sub>e</sub>	ω <sub>e</sub> X <sub>e</sub>	$\alpha_{ m e}$ (10 <sup>-3</sup> )	Ē <sub>e</sub> (10 <sup>−6</sup> )	Te
TcN <sup>−</sup>								
$X^{2}\Delta$	MRCISD	1.6063	129.0	1121.4	4.61	2.78	0.484	0.0
	MRCISD+Q	1.6085	130.9	1118.7	4.61	2.78	0.483	0.0
	RCCSD(T) 1.6104 134.6		134.6	1117.0	4.15	2.80	0.481	0.0
$A^2\Sigma^+$	MRCISD	1.6010	109.5 (150.7)	1136.2	3.13	2.44	0.481	19.4
	MRCISD+Q	1.6024	109.9 (152.4)	1139.3	2.57	2.34	0.476	21.9
	RCCSD(T)	1.6071	112.4 (153.2)	1116.0	4.30	2.61	0.488	22.2
RuC <sup>-</sup>								
$X^{2}\Delta$	MRCISD	1.6473	137.1 (148.9)	1029.0	5.02	3.69	0.732	0.0
	MRCISD+Q	1.6510	142.5 (152.2)	1023.6	4.81	3.70	0.730	0.0
	RCCSD(T)	1.6467	150.2 (152.7)	1040.2	4.32	3.54	0.718	0.0
$A^2\Sigma^+$	MRCISD	1.6173	135.6 [147.3] <sup>c</sup> (182.1) <sup>b</sup>	1090.1	4.81	3.58	0.728	1.4
	MRCISD+Q	1.6210	138.5 [148.0] <sup>c</sup> (183.9) <sup>b</sup>	1084.1	4.82	3.62	0.726	4.2
	RCCSD(T)	1.6169	144.4 [147.0] <sup>c</sup> (178.5) <sup>b</sup>	1103.5	5.09	3.54	0.712	5.7
	B3LYP <sup>d</sup>	1.625	119.5	1152				
RhB <sup>-</sup>								
$X^2\Sigma^+$	MRCISD	1.7012	120.7 (147.3) <sup>f</sup>	914.6	4.40	4.04	0.961	0.0
	MRCISD+Q	1.7051	121.1 (137.1) <sup>f</sup>	911.2	4.44	4.04	0.955	0.0
	RCCSD(T)	1.7100	125.0 (141.1) <sup>f</sup>	906.5	4.06	3.57	0.948	0.0
	TPSSh <sup>e</sup>	1.709		918				
	CCSD(T) <sup>e</sup>	1.712						
	Expt <sup>e</sup>			994(20)				
$A^2\Delta$	MRCISD	1.7905	101.8	778.8	3.94	3.91	0.975	18.9
	MRCISD+Q	1.7944	105.2	777.7	3.93	3.87	0.965	15.9
	RCCSD(T) 1.7906 109.8		109.8	796.1	3.46	3.53	0.932	15.1
$PdBe^{-}$								
$X^2\Sigma^+$	MRCISD	1.9380	51.2	612.0	4.05	5.34	1.686	0.0
	MRCISD+Q	1.9441	56.7	607.9	3.93	5.37	1.677	0.0
	RCCSD(T)	1.9470	55.8	607.5	4.38	5.45	1.664	0.0
$A^2\Delta$	MRCISD	2.2519	16.7	373.5	4.34	5.24	1.840	42.8
	MRCISD+Q	2.2617	21.1	362.9	4.25	5.74	1.897	40.4
	RCCSD(T)	2.2649	22.4	353.3	4.80	6.43	1.985	41.6

Note: Other published data are also included.

<sup>a</sup>Internally contracted MRCI; +Q refers to Davidson correction.

 ${}^{b}\mathsf{D}_{e}{}^{a}\!:$  Adiabatic dissociation energy;  $\mathsf{D}_{e}{}^{d}\!:$  Diabatic dissociation energy.

<sup>c</sup>PECs of RuC<sup>-</sup> correlate adiabatically to Ru + C<sup>-</sup>. In square brackets  $D_e$  with respect to ground states  $Ru^-$  + C products are given.

<sup>d</sup>Ref. [15]; B3LYP/LANL2DZ<sub>Ru</sub>6-311++G(df)<sub>C</sub>.

<sup>e</sup>Ref [10]; TPSSh/aug-cc-pVQZ<sub>B</sub>/ aug-cc-pVQZ-PP<sub>Rh</sub>; CCSD(T)/aug-cc-pVQZ<sub>B</sub> aug-cc-pVQZ-PP<sub>Rh</sub>.

avoided crossings at about 2.5 Å with the excited  ${}^{2}\Delta$  and  ${}^{2}\Sigma^{+}$  states which correlate to Ru<sup>-</sup>(a<sup>4</sup>F; 4d<sup>7</sup>5s<sup>2</sup>) + C(<sup>3</sup>P; 2s<sup>2</sup>2p<sup>2</sup>), see Figure 3. Regarding the A<sup>2</sup>Σ<sup>+</sup> state, an additional avoided crossing occurs at about 2.3 Å, and as a result the bond is formed between Ru<sup>-</sup> (b<sup>4</sup>F; 4d<sup>8</sup>5s<sup>1</sup>) + C(<sup>3</sup>P; 2s<sup>2</sup>2p<sup>2</sup>). Both states present quadruple bonding, i.e.,  $1\sigma^{2}2\sigma^{2} 1\pi^{2}2\pi^{2}$  i.e.,  $5s5p_{z}^{0} \leftarrow 2s^{2}$ ,  $4d_{z2}^{2} \rightarrow 2p_{z}^{0}$ ,  $(4d_{xz}^{\dagger}-2p_{x}^{\downarrow})^{2}$ ,  $(4d_{yz}^{\dagger}-2p_{y}^{\downarrow})^{2}$ , see Scheme 2 and Table S7. It should be noted that the non-bonding  $3\sigma^{2}(X^{2}\Delta)$  and  $3\sigma^{1}(A^{2}\Sigma^{+})$  orbital corresponds to a  $5s5p_{z}$ 

hybridized orbital. The RCCSD(T) bond distances of the  $X^2\Delta$  and  $A^2\Sigma^+$  states are 1.647 and 1.617 Å, about 0.02 Å larger than the corresponding values of  $a^3\Delta(A^1\Delta)$  and  $X^1\Sigma^+$  states of RuC where quadruple bonds are also formed; the attached electron of the anion is added to the  $3\sigma$  orbital.

The potential energy curves of RuC<sup>-</sup> and RuC are depicted in Figures 3 and S4. While in RuC<sup>-</sup> the ground state is a <sup>2</sup> $\Delta$  state and the <sup>2</sup> $\Sigma$ <sup>+</sup> lies 4.2 kcal/mol higher, in the neutral RuC the ordering is

### 1130 WILEY-

**TABLE 3** Electron affinity (A  $\leftarrow$  A<sup>-</sup>, eV) of the Be, B, C, N, Tc, Ru, Rh, Pd atoms and TcN, RuC, RhB, and PdBe molecules at MRCISD, MRCISD+Q, and RCCSD(T)/aug-cc-pV5Z(-PP<sub>M</sub>) levels of theory

	Ве	В	с	Ν	Тс	Ru	Rh	Pd
	$^1S \leftarrow {}^2P$	$^{2}P \leftarrow {}^{3}P$	${}^3\text{P} \leftarrow {}^4\text{S}$	${}^{4}S \leftarrow {}^{3}P$	$^6S \leftarrow {}^5D$	$a {}^{5}F \leftarrow a {}^{4}F$	$a {}^4F \leftarrow a {}^3F$	${}^1S \leftarrow {}^1S$
MRCISD	-0.324	0.149	1.077	-0.478	0.032	0.488	0.525	0.028
MRCISD+Q	-0.254	0.268	1.202	-0.241	0.100	0.792	0.819	0.398
RCCSD(T)	-0.293	0.245	1.238	-0.190	0.310	1.127	0.945	0.479
Expt	-0.5(2) <sup>a</sup>	0.277 <sup>a</sup> 0.279723 <sup>b</sup>	1.2629ª 1.2621226 <sup>c</sup>	-0.07 <sup>a</sup>	0.6 <sup>a</sup> 0.55(20) <sup>d</sup>	1.05°1.04638	e 1.137 <sup>a</sup> 1.14289 <sup>f</sup>	0.557 <sup>a</sup> 0.56214 <sup>f</sup>
	$\begin{array}{l} \text{TcN} \\ \text{X}^1\Delta \leftarrow \text{X}^2\Delta \end{array}$	$\begin{array}{l} RuC \\ X^{1}\Sigma^{+} \leftarrow \end{array}$	X <sup>2</sup> Δ X <sup>1</sup> Σ	$\Sigma^{\star} \leftarrow X^{2}\Sigma^{\star}$	$\begin{array}{l} RhB \\ \alpha^3 \Delta \leftarrow X^2 \Sigma^+ \end{array}$		$A^1\!\Delta \leftarrow X^2\Sigma^{\text{+}}$	$\begin{array}{l} \text{PdBe} \\ \text{X}^1 \Sigma^+ \leftarrow \text{X}^2 \Sigma^+ \end{array}$
MRCISD	0.601 [0.604]	] 0.598 [0.	604] 0.3	85 [0.389]	1.499 [1.5	552]	1.862 [1.909]	0.200 [0.204]
MRCISD+Q	0.914 [0.916]	] 0.947 [0.	954] 0.6	15 [0.620]	1.698 [1.7	750]	2.023 [2.065]	0.438 [0.444]
RCCSD(T)	1.368 [1.375]	] 1.242 [1.	250] 0.8	73 [0.882]	1.959 [1.9	998]		0.743 [0.751]
B3LYP		0.91 <sup>g</sup> , 1	.17 <sup>h</sup>	0.85 <sup>h</sup>				
SO-PBE <sup>i,j</sup> E					1.525, 1.635,	, 1.769 <sup>k</sup>	2.231 <sup>k</sup>	
TPSSh <sup>i,j</sup>				0.968	1.445		2.140	
Expt <sup>i</sup>			C	).961(1) <sup>i</sup>	1.339(1), 1.428(2	l), 1.852(1) <sup>I</sup>	1.852(1) <sup>i</sup>	

Note: In square bracket are given the vertical EA (VEA).

<sup>a</sup>Ref. [27].

<sup>b</sup>Ref. <sup>[28]</sup>.

<sup>c</sup>Ref. <sup>[29]</sup>.

<sup>d</sup>Ref. <sup>[30]</sup>

<sup>e</sup>Ref. [31].

<sup>f</sup>Ref. [32].

<sup>g</sup>Ref. [15]; B3LYP/LANL2DZ<sub>Ru</sub>6-311++G(df)<sub>C</sub>.

<sup>h</sup>Ref. [13]; B3LYP/LANL2DZ; VEA.

<sup>i</sup>Ref. [10], *VDE*.

<sup>j</sup>TPSSh/aug-cc-pVQZ<sub>B</sub>/aug-cc-pVQZ-PP<sub>Rh</sub>; SO-PBE/TZ2P.

 ${}^{k}VEA; \alpha^{3}\Delta_{3} \leftarrow X^{2}\Sigma^{+}: 1.525, \alpha^{3}\Delta_{2} \leftarrow X^{2}\Sigma^{+}: 1.635, \alpha^{3}\Delta_{1} \leftarrow X^{2}\Sigma^{+}: 1.769, A^{1}\Delta_{2} \leftarrow X^{2}\Sigma^{+}: 2.231.$ 

 $^{\text{I}}\text{Expt, VEA: } \alpha^{3}\Delta_{3} \leftarrow X^{2}\Sigma^{\text{+}}\text{: } 1.339(1), \\ \alpha^{3}\Delta_{2} \leftarrow X^{2}\Sigma^{\text{+}}\text{: } 1.428(1), \\ \alpha^{3}\Delta_{1} \leftarrow X^{2}\Sigma^{\text{+}}\text{: } 1.525(6), \\ A^{1}\Delta_{2} \leftarrow X^{2}\Sigma^{\text{+}}\text{: } 1.852(1). \\ A^{1}\Delta_{2} \leftarrow X^{2}\Sigma^{\text{+}}\text{: } 1.852(1).$ 



**FIGURE 1** PECs of the TcN<sup>-</sup> anion at the MRCISD+Q/aug-ccpV5Z(-PP)<sub>M</sub> level of theory; solid points correspond to adiabatic PEC, hollow points correspond to diabatic PEC

reversed, i.e., the ground state is a  ${}^{1}\Sigma^{+}$  state and the  ${}^{3}\Delta$  lies 2.1 kcal/ mol higher. However, in both species the two lowest in energy states are almost energetically degenerate. The binding energies of the X<sup>2</sup> $\Delta$  and  $A^{2}\Sigma^{+}$  states of RuC<sup>-</sup> with respect to correlated [diabatic] products, i.e., Ru(a<sup>5</sup>F) + C<sup>-</sup>(<sup>4</sup>S) [Ru<sup>-</sup>(a<sup>4</sup>F) + C(<sup>3</sup>P)] for X<sup>2</sup> $\Delta$  and Ru<sup>-</sup>(b<sup>4</sup>F) + C (<sup>3</sup>P) for A<sup>2</sup> $\Sigma^{+}$  are 150.2 (152.7) and 144.4 (178.5) kcal/mol, respectively, see Table 2. In the case of the neutral RuC, the  $\Sigma^{+}$  state is the X state. The corresponding binding energies of the X<sup>1</sup> $\Sigma^{+}$ ,  $a^{3}\Delta$ , and A<sup>1</sup> $\Delta$  states of RuC with respect to correlated [diabatic] products, are 165.5 [176.4], 143.8, 150.5 kcal/mol. Thus, the binding energies of anions with respect to the in situ products are bigger than the neutrals by 2 kcal/mol ( $\Sigma^{+}$ ), 9 kcal/mol (<sup>2</sup> $\Delta$  compared to <sup>3</sup> $\Delta$ ) and 2 kcal/mol (<sup>2</sup> $\Delta$  compared to <sup>1</sup> $\Delta$ ). It should be noted that DFT/B3LYP calculation <sup>[15]</sup> predicts the <sup>2</sup> $\Sigma^{+}$  as the ground state and significantly underestimates its binding energy by about 25 kcal/mol, see Table 2.

The EA of Ru was calculated at 1.127 eV in good agreement with experimental measured values of 1.04638(25)<sup>[31]</sup>. The EA of RuC was calculated at 1.242 eV, showing that the bonding further stabilizes the electron attachment. DFT calculations predict lower EA of RuC at 1.17<sup>[13]</sup> and 0.91 eV <sup>[15]</sup>. Comparing RuC with its isovalent FeC, it is observed that they have similar EA, i.e., 1.242 and 1.15 eV <sup>[33]</sup>. However, while in the case of RuC the attached electron is located in Ru, in the case of FeC it is located in C. The ground state of FeC<sup>-</sup> is a  $X^2\Delta$  state, as in the case of RuC<sup>-</sup>, but it correlates to Fe(<sup>5</sup>D; 4d<sup>6</sup>5s<sup>2</sup>) + C<sup>-</sup>(<sup>4</sup>S) and retain this character in its minimum, i.e., the attached



**SCHEME 1** vbL diagram of the  $X^2\Delta$  and  $A^2\Sigma^+$  states of the TcN<sup>-</sup> anion



**FIGURE 2** PECs of the TcN<sup>-</sup> (solid lines) and TcN (dashed lines) species at the MRCISD+Q/aug-cc-pV5Z(-PP)<sub>M</sub> level of theory; solid points correspond to adiabatic PEC, hollow points to diabatic PEC



**FIGURE 3** PECs of the RuC<sup>-</sup> (solid lines) and RuC (dashed lines) species at the MRCISD+Q/aug-cc-pV5Z(-PP)<sub>M</sub> level of theory; solid points correspond to adiabatic PEC, hollow points to diabatic PEC

 $\frac{4d_{x_{1}}}{4d_{y_{2}}} \underbrace{4d_{x_{2}}}_{4d_{y_{2}}} \underbrace{4d_{y_{2}}}_{2p_{1}} \underbrace{2p_{2}}_{2p_{2}} \underbrace{2p_{2}} \underbrace{2p_{2}}_{2p_{2}} \underbrace{2p_{2}} \underbrace{2p_{2}}_$ 



**SCHEME 2** vbL diagram of the  $X^2\Delta$  and  $A^2\Sigma^+$  states of the RuC<sup>-</sup> anion

electron is located in a 2p orbital of C. The EA of FeC is  $1.15 \text{ eV}^{[33]}$  slightly smaller than the EA of the C atom, 1.238 (expt:1.2621)<sup>[29]</sup> eV. Thus, the EA of RuC results from EA of Ru and the bonding enhances it slightly by 0.1 eV, while in the case of FeC the EA results from EA of C and the bonding diminishes it slightly, again by 0.1 eV.

#### 3.1.3 | RhB<sup>-</sup>

In contrast to TcN<sup>-</sup> and RuC<sup>-</sup>, the ground state of RhB<sup>-</sup> is of  $\Sigma^+$  symmetry. Both  $X^2\Sigma^+$  and  $A^2\Delta$  states correlate to Rh<sup>-</sup>(a<sup>5</sup>F; 4d<sup>8</sup>5s<sup>2</sup>) + B(<sup>2</sup>P; 2s<sup>2</sup>2p<sup>1</sup>), see Figure 4. The  $X^2\Sigma^+$  state has an avoided crossing at about 2.7 Å, and as a result the bond is formed between Rh<sup>-</sup>(a<sup>3</sup>D; 4d<sup>9</sup>5s<sup>1</sup>) + B(<sup>2</sup>P), while the  $A^2\Delta$  retains its correlated character in the whole PEC. The quadruple bonding of the states,  $1\sigma^22\sigma^21\pi^22\pi^2$ , cf.,  $(5s5p_z^0 \leftarrow 2s^2) \quad (4d_{zz}^2 \rightarrow 2p_z^0) \quad [(4d_{xz}^{\dagger}-2p_x^{\downarrow})^2 \quad (4d_{yz}^2 \rightarrow 2p_y^0) + (4d_{xz}^2 \rightarrow 2p_x^0) \quad (4d_{yz}^{\dagger}-2p_y^{\downarrow})^2]$  is depicted in Scheme 3, see also Table S7. The non-bonding  $3\sigma^2(A^2\Delta)$  and  $3\sigma^1(X^2\Sigma^+)$  orbital correspond mainly to a 5s orbital, however, there is a  $5s5p_z$  hybridization and the involvement of the 6s Rydberg orbital. The quadruple bonding in the ground  $X^2\Sigma^+$  state of RhB<sup>-</sup> was first reported by Cheung et al. <sup>[10]</sup> who studied it via photoelectron spectroscopy and CCSD(T)/aug-cc-pVQZ\_B(-PP\_Rh).

The bond distances of the  $X^2\Sigma^+$  and  $A^2\Delta$  states are 1.705 and 1.794 Å, about 0.03 Å larger than the corresponding values of the  $X^1\Sigma^+$  and  $a^3\Delta(A^1\Delta)$  states of RhB. The PEC of RhB<sup>-</sup> and RhB are shown in Figure 4 and in Figure S5. The binding energies of the  $X^2\Sigma^+$ and  $A^2\Delta$  states of RhB<sup>-</sup> with respect to the adiabatic [diabatic for  $X^2\Sigma^+$ ] products are 125.0 [141.1] and 109.8 kcal/mol, respectively, see Table 2, while the corresponding D<sub>e</sub> values of the  $X^1\Sigma^+$ ,  $a^3\Delta$ , and  $A^1\Delta$  states of RhB are 135.1, 101.2, 102.6 [107.4] kcal/mol. Thus, the binding energies of anions with respect to the in situ products are bigger than the neutrals by 6 kcal/mol ( $\Sigma^+$ ), 9 kcal/mol ( $^2\Delta$  compared to  $^3\Delta$ ) and 2 kcal/mol ( $^2\Delta$  compared to  $^1\Delta$ ). Finally, it should be noted that the  $X^1\Sigma^+$  of RhB and  $A^2\Delta$  are close lying within 0.2 eV, see Figure 4.



**FIGURE 4** PECs of the RhB<sup>-</sup> (solid lines) and RhB (dashed lines) species at the MRCISD+Q/aug-cc-pV5Z(-PPp)<sub>M</sub> level of theory; solid points correspond to adiabatic PEC, hollow points to diabatic PEC



**SCHEME 3** vbL diagram of the  $X^2\Sigma^+$  and  $A^2\Delta$  states of the RhB<sup>-</sup> anion

The calculated RCCSD(T) EA of Rh and RhB are 0.945 and 0.873 eV, respectively, in good agreement with the experimental values of  $1.137^{[27]}$  and  $1.14289 \text{ eV}^{[32]}$  for Rh and  $0.961(1)^{[10]}$  eV for RhB measured via photoelectron spectroscopy. In contrast to TcN and RuC, the EA of RhB is lower than the Rh, showing that the bonding is slightly de-stabilized by 0.1 eV theoretically and by 0.2 eV experimentally.

#### 3.1.4 | PdBe<sup>-</sup>

The  $X^{2}\Sigma^{+}$  and  $A^{2}\Delta$  states correlate to  $Pd^{-}(^{2}S; 4d^{10}5s^{1})$  and  $Pd^{-}(^{2}D; 4d^{9}5s^{2}) + Be(^{1}S; 2s^{2})$ , respectively, see Figure 5, and they retain their correlated character in their whole PEC.  $X^{2}\Sigma^{+}$  has a clear quadruple bonding,  $1\sigma^{2}2\sigma^{2}1\pi^{2}2\pi^{2}$ , i.e.,  $5s5p_{z}^{0} \leftarrow 2s^{2}$ ,  $4d_{z2}^{2} \rightarrow 2p_{z}^{0}$ ,  $4d_{xz}^{2} \rightarrow 2p_{x}^{0}$ ,  $4d_{yz}^{2} \rightarrow 2p_{y}^{0}$ , while in the singly  $3\sigma^{1}$  occupied a  $5s5p_{z}4d_{z2}$  hybridization is clearly observed, see Table S7. In the  $A^{2}\Delta$  the two  $\pi$  bonds are less strong than in  $X^{2}\Sigma^{+}$  showing that the bonding is mainly  $1\sigma^{2}2\sigma^{2}$ , i.e.,  $5sp_{z}^{0} \leftarrow 2s^{2}$ ,  $4d_{z2}^{2} \rightarrow 2p_{z}^{0}$ , the  $3\sigma^{2}$  is a  $5s^{2}$ 



**FIGURE 5** PECs of the PdBe<sup>-</sup> anion at the MRCISD+Q/aug-ccpV5Z(-PP)<sub>M</sub> level of theory; solid lines adiabatic PEC, dashed lines diabatic PEC



**SCHEME 4** vbL diagram of the  $X^2\Sigma^+$  and  $A^2\Delta$  states of the PdBe<sup>-</sup> anion

orbital which also interact with  $2sp_z$  hybridized orbital of Be. The involvement of the 6s Rydberg orbital is not observed as in the case of RhB<sup>-</sup>. The bonding is depicted in Scheme 4.

The bond distances of the  $X^2\Sigma^+(X^1\Sigma^+)$  and  $A^2\Delta(b^3\Delta, A^1\Delta)$  states of PdBe<sup>-</sup> (PdBe) are 1.944 (1.912) and 2.262 (2.147, 2.132) Å, i.e., the anion presents elongated bond distances compared to the neutral by about 0.03 Å for the  $\Sigma^+$  states and significantly larger by 0.12 Å for the  $\Delta$  states. The PEC of PdBe<sup>-</sup> and PdBe are shown in Figures 5 and S6, where it is depicted that the  $X^1\Sigma^+$  of the neutral molecule is significantly lower in energy, by 1.06 eV, than the first excited states  $A^2\Delta$  state of the anion. The binding energies of the  $X^2\Sigma^+$  ( $X^1\Sigma^+$ ) and  $A^2\Delta$  ( $b^3\Delta$ ,  $A^1\Delta$ ) states of PdBe<sup>-</sup> (PdBe) are 56.7 (52.8 <sup>[11]</sup>) and 21.1 (24.2, 29.1) <sup>[11]</sup> kcal/mol, respectively, see Table 2. Thus, the binding energy of the  $^2\Sigma^+$  state of anion is larger than the molecule by 4 kcal/mol, while the opposite occurs for the  $\Delta$  states. It should be noted that it was possible to obtain the PEC at the RCCSD(T) level of theory, see Figure S6, because all bonds are dative, thus the PEC can open correctly to the in situ products. The calculated RCCSD(T) EA of Pd and PdBe are 0.479 and 0.743 eV, respectively. There is a good agreement with the available experimental EA value of Pd, which was measured at 0.557 <sup>[27]</sup> and 0.56214 eV <sup>[32]</sup>. As in the cases of TcN and RuC, the EA of PdBe is lower than that of Pd, showing that the bonding further stabilizes the anion.

#### 3.2 | Comparisons between MX<sup>-</sup> and MX species

#### 3.2.1 | Bond distances

It is interesting that even though both MX<sup>-</sup> and MX species involve metals with large atomic number, i.e., 43-46, their bond distances are small and range from 1.558 to 1.944 Å as a consequence of the formation of quadruple bonds. The plots of bond distances (R<sub>e</sub>) of the  ${}^{2}\Sigma^{+}$  and  ${}^{2}\Delta$  states of MX<sup>-</sup> and  ${}^{1}\Sigma^{+}$ ,  ${}^{3}\Delta$ , and  ${}^{1}\Delta$ of MX as the atomic number increases are given in Figures 6A and S7. In TcN<sup>-,0</sup> three bonds are covalent and one is dative, while in PdBe<sup>-,0</sup> all bonds are dative. The differences in R<sub>e</sub> occur because the number of covalent bonds decreases and subsequently the number of dative bonds increases. Comparing the corresponding  $\Sigma^+$  and  $^2\Delta$  states of anions and neutrals, the R<sub>e</sub> of the anions are slightly elongated, i.e., by 0.01 Å (TcN<sup>-,0</sup>), 0.02 Å (RuC<sup>-,0</sup>), 0.03 Å (RhB<sup>-,0</sup>) and 0.03 Å (PdBe<sup>-,0</sup> for the  $\Sigma^+$  states). Note that, the  $\Delta$ states of PdBe<sup>-,0</sup> do not form guadruple bonds and as a result the difference of their R<sub>e</sub> between neutral and anion is large enough, namely ~0.12 Å.

# 

1133

3.2.2 | Dissociation energies

The plots of the dissociation energies (D\_e) of the  $^2\Sigma^+$  and  $^2\Delta$  states of  $MX^-$  and  $^1\Sigma^+,\,^3\Delta,$  and  $^1\Delta$  of MX as the atomic number increases are depicted in Figures 6, S9 and S10. Generally, both neutral MX and anionic  $MX^-$  species present similar plots for  $D_e^{a}$  and  $D_e^{d}$  with respect to the atomic number of M. Regarding the  $\Sigma^+$  states, the MRCISD+Q  $D_e^a$  values of MX<sup>-</sup> range from 57 to 139 kcal/mol, while their  $D_e^d$ values reach up to 184 kcal/mol. For the neutrals, their De<sup>a</sup> range from 53 to 166 kcal/mol, while their Ded values reach up to 176 kcal/ mol, see Table 2 and Figure 6B,C. As it is shown in Figure 6, the MX molecules present larger  $\mathsf{D}_{e}^{\;a}$  values than  $\mathsf{MX}^{-}$  for Tc-Rh and this trend is reversed for Pd. It is of interest that the difference in Dea values decreases from Tc to Pd, namely the differences range form 27 to -4 kcal/mol. On the contrary, both MX and MX<sup>-</sup> present similar  $\mathsf{D_e}^d$  values for their  $\Sigma^+$  states, the anionic species present larger  $\mathsf{D_e}^d$ values up to 7 kcal/mol, i.e., the attachment of an electron slightly enhances the energy bonding. Regarding the  $\Delta$  states, with exception of Pd, the  $^{2}\Delta$  states of MX<sup>-</sup> have larger D<sub>e</sub> values than  $^{1}\Delta$  and  $^{3}\Delta$  of MX. The largest differences are observed with the  ${}^{3}\Delta(MX)$ , i.e., up to 11 kcal/mol ( $^{3}\Delta$  and  $^{2}\Delta$  of Tc). Thus, the electron attachment further stabilizes the  $\Delta$  states. For Pd, the neutral has a larger  $D_e^a$  value for its  $\Delta$  states up to 9 and a larger  $D_e^{d}$  value up to 66 kcal/mol, see Figure 6C.

Finally, it should be mentioned that the ground and first excited states,  ${}^{2}\Sigma^{+}$  and  ${}^{2}\Delta$ , of TcN<sup>-</sup>, RhB<sup>-</sup>, and PdBe<sup>-</sup> correlates adiabatically to M<sup>-</sup> + X, while those of RuC<sup>-</sup> correlate adiabatically to Ru + C<sup>-</sup>, due to larger EA of C compared to Ru.



**FIGURE 6** (a) Bond distance, R<sub>e</sub>, (b) adiabatic dissociation energy  $D_e^a$ , (c) diabatic dissociation energy  $D_e^d$ , (d) frequency  $\omega_e$  and (e) relative energy T<sub>e</sub> of MX<sup>-</sup> and MX at MRCISD+Q (solid lines) and RCCSD(T)(dashed lines)/aug-cc-pV5Z(-PP)<sub>M</sub> level of theory; (f) relative energy levels (T<sub>e</sub>) of the <sup>2</sup> $\Delta$  states of the MX<sup>-</sup> anions with respect to the <sup>2</sup> $\Sigma^+$  at MRCISD, MRCISD+Q, and RCCSD(T)/aug-cc-pV5Z<sub>x</sub>(-PP)<sub>M</sub>

1134 WILEY Control of ULTATIONAL

#### 3.2.3 | Frequencies

The harmonic frequencies  $\omega_e$  of the  $^2\Sigma^+$  and  $^2\Delta$  states of MX<sup>-</sup> decrease from Tc to Pd, see Figures 6D and S8. TcN<sup>-</sup> and RuC<sup>-</sup> anions have similar  $\omega_e$  values. RuC<sup>-</sup> presents slightly smaller values than TcN<sup>-</sup>. PdBe<sup>-</sup> is the least rigid anion; its  $\omega_e$  values are smaller by 46% ( $^{2}\Sigma^{+}$ ) and 68% ( $^{2}\Delta$ ) than those of TcN<sup>-</sup>. As the atomic number of the metals increases, the difference of  $\omega_{\text{e}}$  values between the two states increases. Comparing the  $\omega_{e}$  values of the anions with those of the neutral molecules, the shape of the curve of  $\omega_{e}$  with respect to the species is the same. It is interesting that the  $\omega_e$  values of  ${}^{2}\Sigma^{+}$  state of MX<sup>-</sup> at RCCSD(T) level are smaller by about 30 cm<sup>-1</sup> than the corresponding values of  $\omega_e$  values of  ${}^{1}\Sigma^{+}$  state of MX. Comparing the corresponding  $\omega_e$  values of the  $^2\Delta$  states of MX<sup>-</sup> with  $\omega_e$  of  $^3\Delta$  and  $^1\Delta$ of MX, they are smaller by about 20 and 40  $cm^{-1}$  with the exception of PdBe<sup>0,-</sup> species, where the differences are significant smaller, i.e., about 100 and 120 cm<sup>-1</sup> respectively, showing a different type of bond between  $\Delta$  states of PdBe<sup>-</sup> and PdBe.

#### 3.2.4 | Relative energies

The relative energy levels of the  ${}^{2}\Delta$  states of the MX<sup>-</sup> anions with respect to the  ${}^{2}\Sigma^{+}$  at all calculated levels of theory are depicted in Figures 6F, S11 and S12. The relative ordering of the two states is maintained for each anion at all levels of theory. For the PdBe<sup>-</sup> anion, its ground state is a  ${}^{2}\Sigma^{+}$  state, while its  ${}^{2}\Delta$  state lies 41.6 kcal/mol higher. As the atomic number of the metal decreases, the energy difference also decreases, i.e., at 15.1 kcal/mol for RhB<sup>-</sup>, while the ordering is reversed at -5.7 kcal/mol for RuC<sup>-</sup> and it reaches at -22.2 kcal/mol for TcN<sup>-</sup>. This reversing occurs because of the different energy separation of the atomic states of the metal anions involved in the  ${}^{2}\Sigma^{+}$  and  ${}^{2}\Delta$  states which is diminished from Tc<sup>-</sup> to Rh<sup>-</sup>. Note that the atomic state of the metal anion involved in the  ${}^{2}\Sigma^{+}$ 

state is higher in energy than the one involved in the  ${}^{2}\Delta$  for Tc<sup>-</sup>, Ru<sup>-</sup>, and Rh<sup>-</sup>; their RCCSD(T) energy differences are: 1.769 eV [Tc<sup>-:</sup>  ${}^{5}F$  $(4d^{7}5s^{1}) \leftarrow {}^{5}D(4d^{6}5s^{2})]$ , 1.365 eV [Ru<sup>-</sup>:  $b^{4}F$  ( $4d^{8}5s^{1}) \leftarrow a^{4}F(4d^{7}5s^{2})]$ , and 0.697 eV [Rh<sup>-</sup>:  $a^{3}D$  ( $4d^{9}5s^{1}) \leftarrow a^{3}F(4d^{8}5s^{2})]$ , see Table 1. On the contrary, in PdBe<sup>-</sup> the atomic state of the Pd<sup>-</sup> involved in the  ${}^{2}\Sigma^{+}$  is the lowest one, i.e.,  $a^{2}S$  (an energy difference of 0.357 eV corresponds to [Pd<sup>-</sup>:  $a^{2}D(4d^{9}5s^{2}) \leftarrow a^{2}S(4d^{10}5s^{1})]$ ), and as a result its X<sup>2</sup>Σ<sup>+</sup> is significant lower in energy than the  ${}^{2}\Delta$  state (41.6 kcal/mol), see Table 2.

Similarly, in the neutral species, the relative energy difference between  ${}^{1}\Sigma^{+}$  and  ${}^{3}\Delta$  results from the different energy separation of the atomic states of metals involved in the states.<sup>[11]</sup> The relative energy of the lowest  ${}^{2}\Delta$  and  ${}^{1,3}\Delta$  states of MX<sup>-</sup> and MX species with respect to the  ${}^{2}\Sigma^{+}(MX^{-})$  and  ${}^{1}\Sigma^{+}(MX)$  states are depicted in Figure 6E. We observe that the  ${}^{2}\Delta$  states lie lower that than the  ${}^{3}\Delta$  states, showing that the attachment of an electron further stabilized the  $\Delta$  states. As a result, among the neutrals species only for TcN the ground state is a  $\Delta$  state is a  $\Delta$  one.

#### 3.2.5 | Bonding

As mentioned above quadruple bonding is formed in MX<sup>-</sup> which fulfill the necessary requirements for the occurrence of quadruple bonds, i.e., (i) existence of low-lying atomic states having low lying unoccupied orbitals that can receive electrons via dative bonds and (ii) atoms with doubly occupied orbitals that can form dative bonds. The bonding for all MX<sup>-</sup> is depicted pictorially via a concise valence bond Lewis (vbL) diagram and via 3D contour plots of the valence molecular orbitals (MO), see Figure 7. Note that the vbL diagrams provide a compact representation of the 3D valence MO. Similar 3D orbital contour plots are observed for all MX<sup>-</sup>, see Figures S14 and S15. It is observed that the 5s orbital of M present a small polarization out of



**FIGURE 7** Molecular orbitals of the  ${}^{2}\Sigma^{+}$  and  ${}^{2}\Delta$  states presenting quadruple bonds. (the plotted 3D orbital contours correspond to RuC<sup>-</sup> molecule, which are similar with the 3D orbital contours of the TcN<sup>-</sup>, RhB<sup>-</sup>, and PdBe<sup>-</sup>, see Figures S14 and S15)

the M-X bond region to minimize Pauli repulsion with the  $\sigma$  bond. Comparing the quadruple bonding of  $MX^-$  with MX, in the  $\Sigma^+$  states, the  $2\sigma^2$  bond changes from  $5s^0 \leftarrow 2s^2$  in  ${}^{1}\Sigma^{+}(MX)$  to  $5p_z{}^0 \leftarrow 2s^2$  in  $^{2}\Sigma^{+}(MX^{-})$  because the attached electron is located at the empty 5s orbital of the M of  $\Sigma^+$  and as a result the 5p<sub>7</sub> is preferred for the dative bond. However, there is intense 5s5p<sub>7</sub> hybridization for Ru<sup>-</sup>, Rh<sup>-</sup>and Pd<sup>-</sup>. In  $\Delta$  states, the attached electron is located at the semi-occupied 5s and the quadruple character of the bonding does not change because the 5s orbital is not mainly involved in the bonding of MX. Both Mulliken and NBO population analyses confirm the bonding. Although, there are differences between the two analyses regarding the total charge of metal, c.f., the Mulliken analysis provides more negative charge (see Table S4), subtracting the population analysis of neutral MX from the one of MX<sup>-</sup> within  $\Sigma^+$  and  $\Delta$  states results in similar data for both analyses (see Table S5). The attached electron is located in a 5s orbital of M<sup>-</sup>, however, the Rydberg 6s orbital is also involved mainly in the case of RhB<sup>-</sup>. Moreover, comparing neutrals with anions, the hybridization 5s5p<sub>7</sub> is more intense in anions and the 5p<sub>7</sub> gains about 0.2 e<sup>-</sup>. In the case of PdBe<sup>-</sup>, the charge of 2s of Be is also increased by about 0.4 e<sup>-</sup> comparing to 2s of Be in neutral PdBe. Finally, it should be noted that valence bond calculations can also provide significant insight in the bonding analysis <sup>[34],</sup> however, some convergence problems were appeared for the present calculated systems.

As in the case of the MX<sup>-</sup> and MX species <sup>[10,11],</sup> a quadruple motif has also been reported for C<sub>2</sub> molecule,<sup>[9]</sup> even though some research groups have different interpretation for the nature of the two  $\sigma$  bonds, i.e., regarding the atomic state of the C atoms.<sup>[9]</sup> However, here, as in the case of C<sub>2</sub>, the two  $\sigma$  bonds can be regarded as a strong inner  $\sigma$  bond (4d<sub>z2</sub> - 2p<sub>z</sub>)<sup>2</sup> and a weak outer  $\sigma$  bond 5p<sub>z</sub><sup>0</sup>  $\leftarrow$  2s<sup>2</sup>.

#### 3.2.6 | Electron affinities

The EA of X, M and MX, are given in Table 3 and they are depicted in Figures 8 and S13. There is a good agreement between theory and

the available experimental data, see Figure 8. The RCCSD(T) values are in better agreement with the experimental data than the MRCISD ones, except for Be. Regarding the MX species, only for RhB has EA been measured experimentally at 0.961 eV, i.e., in good agreement with the RCCSD(T) value of 0.873 eV. Comparing the EA of the involved fragments of the MX<sup>-</sup> anions, we observe that the EA of the metals are larger than those of the corresponding main group elements with the exception of Ru, which is smaller than C. The EA of MX ranges from 0.743 to 1.368 eV. It should be noted that as the atomic number of the metal increases, the EA of the corresponding MX decreases. Thus, species with metal owning fewer electrons have larger attachment energy. The EA of TcN is significantly larger than Tc because in the case of TcN<sup>-</sup> the detached e<sup>-</sup> is an s<sup>1</sup> electron, while in the case of Tc is a d electron, which is more loosely bound, see Tables 1 and 3. The EAs of RhB and PdBe are similar to their corresponding metals, i.e., within 0.2 eV, because in both cases the detached e<sup>-</sup> is an s<sup>1</sup> electron for both MX<sup>-</sup> and M<sup>-</sup>. However, in Pd<sup>-</sup>, PdBe<sup>-</sup>, and RhB<sup>-</sup> the detached electron comes from a semi-occupied s orbital, while in Rh<sup>-</sup> the e<sup>-</sup> is detached from a fully occupied s<sup>2</sup>. Finally, in RuC<sup>-</sup>, the detached electron comes from a 5s<sup>2</sup> orbital, while the other 5s e<sup>-</sup> moves to a d orbital; in contrast, in Ru<sup>-</sup> the detached  $e^{-}$  comes from a fully occupied 5s<sup>2</sup> orbital.

To sum up, the RCCSD(T) energy levels of the low-lying states of the MX<sup>-</sup> and MX species with respect to the ground states of MX<sup>-</sup> are shown in Figure 9; the good agreement with the available experimental EA value of RhB is also shown. The bonds from TcN<sup>-,0</sup> to PdBe<sup>-,0</sup> gradually change from covalent to dative bonds resulting to an increase of bond distances, decrease of frequency ( $\omega_e$ ), decrease of binding energies (with the exception of RuC<sup>-,0</sup>) and a decrease of EA of MX. Finally, states of neutral, which lie up to 2.28 eV higher the ground state of MX<sup>-</sup>, present quadruple bonding. Note that this property of the calculated MX<sup>-,0</sup> molecules to form quadruple bonds in their ground and excited states results from the fact the M transition metals and M<sup>-</sup> anions have low lying in energy 5s and 5p<sub>z</sub> unoccupied orbitals that can receive electrons via dative bonds.



**FIGURE 8** EA of M, X, and MX at the RCCSD(T)/aug-cc-pV5Z (-PP)<sub>M</sub> level of theory



**FIGURE 9** Relative energy levels ( $T_e$ ) of the energy states of the MX<sup>-</sup> and MX species with respect to the ground states of MX<sup>-</sup> at the RCCSD(T)/aug-cc-pV5Z<sub>X</sub>(-PP)<sub>M</sub> level of theory

1136 WILEY Control of ULEINAL

#### 4 | CONCLUSIONS

In the present study, it is found that the isoelectronic TcN<sup>-</sup>, RuC<sup>-</sup>, RhB<sup>-</sup>, and PdBe<sup>-</sup> anions present quadruple bonding. Their two lowest  $^{2}\Delta$  and  $^{2}\Sigma^{+}$  electronic states were studied via MRCISD (MRCISD+Q) and RCCSD(T) methodologies. Bond distances, diabatic and adiabatic dissociation energies and spectroscopic parameters were computed. Additionally, the effect of the electron attachment on the calculated spectroscopic data of MX was studied and the influence of the involved atomic states on calculated data was also analyzed. Finally, the EAs of the neutral MX were calculated.

Here, it is found that the four MX<sup>-</sup> anions form quadruple bonds in their ground states ( $X^2\Delta$  or  $X^2\Sigma^+$ ) and in the first excited states ( $A^2\Sigma^+$  or  $A^2\Delta$ ) of TcN<sup>-</sup>, RuC<sup>-</sup>, RhB<sup>-</sup>. The attached electron is located at the empty 5s orbital of the M of  $\Sigma^+$ ; as a result, the  $2\sigma^2$  bond changes from  $5s^0 \leftarrow 2s^2$  in  ${}^1\Sigma^+$ (MX) to  $5p_z^0 \leftarrow 2s^2$  in  ${}^2\Sigma^+$ (MX<sup>-</sup>), while an intense  $5s5p_z$  hybridization exists for Ru<sup>-</sup>, Rh<sup>-</sup>and Pd<sup>-</sup> anions. In  $\Delta$ states, the attached electron is located at the semi-occupied 5s and the quadruple character of the bonding does not change because the 5s orbital is not mainly involved in the bonding of MX. Moving from TcN<sup>-</sup> to PdBe<sup>-</sup>, the number of covalent bonds decreases, i.e., TcN<sup>-</sup> has three covalent bonds and one dative, while in PdBe<sup>-</sup> all four bonds are dative. Strong bonding results in short bond length, despite the large atomic number of metals involved. Bond distances of the lowest states range from 1.602 (TcN<sup>-</sup>) to 1.944 Å (PdBe<sup>-</sup>).

Regarding the  ${}^{2}\Sigma^{+}$  states of MX<sup>-</sup>, their adiabatic dissociation energies  $D_{e}^{a}$  range from 57 to 139 kcal/mol, while their diabatic  $D_{e}^{d}$ values reached up to 184 kcal/mol. The MX molecules present larger  $D_{e}^{a}$  values than MX<sup>-</sup>, expect for Pd; the difference in  $D_{e}^{a}$  values decreases from Tc to Rh. On the contrary, both MX and MX<sup>-</sup> present similar  $D_{e}^{d}$  values, cf., the attachment of an electron slightly enhances the diabatic binding energy. Regarding the  ${}^{2}\Delta$  states,  $D_{e}^{a}$  values range from 21 to 142 kcal/mol. Apart from Pd,  ${}^{2}\Delta$  states of MX<sup>-</sup> have larger  $D_{e}$  values than  ${}^{1,3}\Delta$  of MX, i.e., the electron attachment further stabilizes the  $\Delta$  states.

The EA of MX were calculated at 1.368 (TcN), 1.242 (RuC), 0.873 (RhB), and 0.743 eV (PdBe). Only for RhB has EA been measured experimentally at 0.961 eV, i.e., in good agreement with the calculated value of 0.873 eV. The EAs of RhB and PdBe are similar to their corresponding metals, i.e., within 0.2 eV, because in both cases the attached e<sup>-</sup> is a  $5s^1$  electron for both MX and M. On the contrary, the EA of TcN is significantly larger than Tc because in the case of TcN the attached e<sup>-</sup> is a  $5s^1$  electron, while in the case of Tc, it is a loosely bound 4d electron.

To sum up, both MX<sup>-</sup> and MX present similar bond distances, diabatic and adiabatic dissociation energies and spectroscopic parameters due to their quadruple bonding. Furthermore, while, quadruple bonding is not commonly found for the main group elements of the second period, they can form such bonds with the appropriate "partner" which should have low-lying unoccupied orbitals that can receive a pair of electrons as 2nd row transition metals do. Finally, given the surprising lack of information on MX<sup>-</sup> anions in the literature, the present study provides experimentalists with useful data for future studies.

#### ACKNOWLEDGMENT

DT acknowledges the National and Kapodistrian University of Athens, Special Accounts for Research Grants for supporting this work through the project "SONFM" (KE 17034).

#### DATA AVAILABILITY STATEMENT

The data generated during this study are available within the article and its supporting information.

#### ORCID

Demeter Tzeli D https://orcid.org/0000-0003-0899-7282

#### REFERENCES

- N. N. Greenwood, A. Earnshaw, Chemistry of the Elements, 2nd ed., Elsevier, Oxford 2014.
- [2] J. K. McCusker, Science 2019, 363, 484.
- [3] P. J. Robinson, G. Liu, S. Ciborowski, C. Martinez-Martinez, J. R. Chamorro, X. Zhang, T. M. McQueen, K. H. Bowen, A. N. Alexandrova, *Chem. Mater.* 2017, 29, 9892.
- [4] R. Gramage-Doria, C. Bruneau, Coord. Chem. Rev. 2021, 428, 213602.
- [5] E. Latocheski, G. M. Dal Forno, T. M. Ferreira, B. L. Oliveira, G. J. L. Bernardes, J. B. Domingos, *Chem. Soc. Rev.* 2020, 49, 7710.
- [6] E. B. Clatworthy, S. V. Konnov, F. Dubray, N. Nesterenko, J.-P. Gilson, S. Mintova, Angew. Chem., Int. Ed. 2020, 59, 19414.
- [7] L. Wang, Y. Li, L. Zhao, Z. Qi, J. Gou, S. Zhang, J. Z. Zhang, Nanoscale 2020, 12, 19516.
- [8] D. Tzeli, A. Mavridis, J. Chem. Phys. 2008, 128, 034309.
- [9] a) J. Grunenberg, Nat. Chem. 2012, 4, 154. b) S. Shaik, H. S. Rzepa, R. Hoffmann, Angew. Chem., Int. Ed. 2013, 52, 3020. c) D. Danovich, P. C. Hiberty, W. Wu, H. S. Rzepa, S. Shaik, Chem. Eur. J. 2014, 20, 6220. d) L. T. Xu, T. H. Dunning, J. Chem. Theory Comput. 2014, 10, 195. e) M. Hermann, G. Frenking, Chem. Eur. J. 2016, 22, 4100. f) S. Shaik, D. Danovich, B. Braida, P. C. Hiberty, Chem. Eur. J. 2016, 22, 4116. g) D. W. O. de Sousa, M. A. C. Nascimento, J. Chem. Theory Comput. 2016, 12, 2234.
- [10] L. F. Cheung, T.-T. Chen, G. S. Kocheril, W.-J. Chen, J. Czekner, L.-S. Wang, J. Phys. Chem. Lett. 2020, 11, 659.
- [11] D. Tzeli, I. Karapetsas, J. Phys. Chem. A 2020, 124, 6667.
- [12] L. F. Cheung, G. S. Kocheril, J. Czekner, L.-S. Wang, J. Chem. Phys. 2020, 152, 174301.
- [13] B. Kharat, S. B. Deshmukh, A. Chaudhari, Int. J. Quantum Chem. 2009, 109, 1103.
- [14] A. C. Borin, J. P. Gobbo, J. Phys. Chem. A 2009, 113, 12421.
- [15] J. Wang, X. Sun, Z. Wu, Chem. Phys. Lett. 2006, 426, 141.
- [16] a) R. Scullman, B. Thelin, Phys. Scr. 1972, 5, 201. b) A. Lagerqvist, H. Neuhaus, R. Scullman, Z. Naturforsch. A 1965, 20, 751. c) N. S. McIntyre, A. Vander Auwera-Mahien, J. Drowart, Trans. Faraday Soc. 1968, 64, 3006. d) K. A. Gingerich, Chem. Phys. Lett. 1974, 75, 523. e) R. Scullman, B. Thelin, Phys. Scr. 1971, 3, 19. f) I. Shim, H. C. Finkbeiner, K. A. Gingerich, J. Phys. Chem. 1987, 91, 3171. g) I. Shim, K. A. Gingerich, Surf. Sci. 1985, 156, 623. h) I. Shim, K. A. Gingerich, Chem. Phys. Lett. 2000, 317, 338. i) R. Guo, K. Balasubramanian, J. Chem. Phys. 2004, 120, 7418.
- [17] a) T. C. Steimle, W. L. Virgo, J. M. Brown, J. Chem. Phys. 2003, 118, 2620. b) W. L. Virgo, T. C. Steimle, L. E. Aucoin, J. M. Brown, Chem. Phys. Lett. 2004, 391, 75.
- [18] a) J. D. Langenberg, R. S. DaBell, L. Shao, D. Dreessen, M. Morse, J. Chem. Phys. **1998**, 109, 7863. b) R. S. DaBell, R. G. Meyer, M. D. Morse, J. Chem. Phys. **2001**, 114, 2938. c) N. F. Lindholm, D. A. Hales, L. A. Ober, M. D. Morse, J. Chem. Phys. **2004**, 121, 6855.
- [19] a)A. V. Auwera-Mahieu, R. Peeters, N. S. McIntyre, J. Drowart, Trans. Faraday Soc. 1970, 66, 809. b) P. K. Chowd-hury, W. J. Balfour,

J. Chem. Phys. **2006**, 124, 216101. c) D. M. Merriles, E. Tieu, M. D. Morse, J. Chem. Phys. **2019**, 151, 044302. d) P. K. Chowdhury, W. J. Balfour, *Mol. Phys.* **2007**, 105, 1619. e) A. C. Borin, J. P. Gobbo, J. Phys. Chem. A **2008**, 112, 4394.

- [20] a) B. P. Prascher, D. E. Woon, K. A. Peterson, T. H. Dunning, A. K. Wilson, *Theor. Chem. Acc.* 2011, 128, 69. b) T. H. Dunning, *J. Chem. Phys.* 1989, 90, 1007. c) R. A. Kendall, T. H. Dunning, R. J. Harrison, *J. Chem. Phys.* 1992, 96, 6796.
- [21] K. A. Peterson, D. Figgen, M. Dolg, H. Stoll, J. Chem. Phys. 2007, 126, 124101.
- [22] H.-J. Werner, P. J. Knowles, J. Chem. Phys. 1988, 89, 5803.
- [23] S. R. Langhoff, E. R. Davidson, Int. J. Quantum Chem. 1974, 8, 61.
- [24] P. J. Knowles, C. Hampel, H.-J. Werner, J. Chem. Phys. **1993**, *99*, 5219.
- [25] D. Tzeli, A. Mavridis, J. Chem. Phys. 2002, 116, 4901.
- [26] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani; W. Györffy, D. Kats, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, and M. Wang MOLPRO 2015.1, a package of ab initio programs.
- [27] S. G. Bratsch, J. J. Lagowski, Polyhedron 1986, 5, 1763.

[28] M. Scheer, R. C. Bilodeau, H. K. Haugen, Phys. Rev. Lett. 1998, 80, 2562.

UTATIONAL -WILEY

1137

- [29] a) D. Bresteau, C. Drag, C. Blondel, Phys. Rev. A 2016, 93, 013414. b)
   M. Scheer, R. C. Bilodeau, C. A. Brodie, H. K. Haugen, Phys. Rev. A 1998, 58, 2844.
- [30] W. M. Haynes, CRC Handbook of Chemistry and Physics, 92nd ed., CRC Press, Boca Raton, FL 2011-2012.
- [31] P. L. Norquist, D. R. Beck, R. C. Bilodeau, M. Scheer, R. A. Srawley, H. K. Haugen, *Phys. Rev. A* **1999**, *59*, 1896.
- [32] M. Scheer, C. A. Brodie, R. C. Bilodeau, H. K. Haugen, Phys. Rev. A 1998, 58, 2051.
- [33] D. Tzeli, A. Mavridis, J. Chem. Phys. 2010, 132, 194312.
- [34] κ. Hirao, H. Nakano, K. Nakayama, J. Chem. Phys. 1996, 105, 9227.

#### SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Tzeli D. Quadruple chemical bonding in the diatomic anions TcN<sup>-</sup>, RuC<sup>-</sup>, RhB<sup>-</sup>, and PdBe<sup>-</sup>. *J Comput Chem*. 2021;42:1126–1137. <u>https://doi.org/10.</u> 1002/jcc.26527