

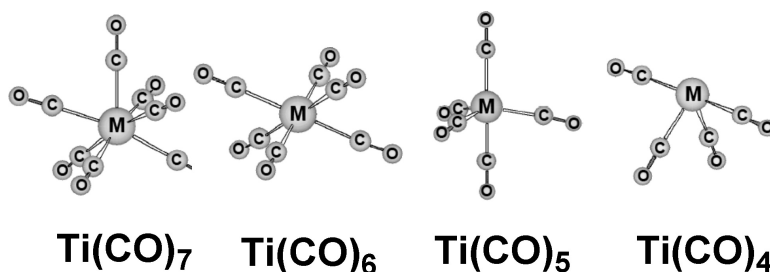
Article

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*J. Am. Chem. Soc.*, **2008**, 130 (24), 7756-7765 • DOI: 10.1021/ja8003655 • Publication Date (Web): 21 May 2008

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## Bonding of Seven Carbonyl Groups to a Single Metal Atom: Theoretical Study of $M(\text{CO})_n$ ( $M = \text{Ti, Zr, Hf}$ ; $n = 7, 6, 5, 4$ )

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**Abstract:** The equilibrium geometries, thermochemistry, and vibrational frequencies of the homoleptic metal–carbonyls of the group 4 elements,  $M(\text{CO})_n$  ( $M = \text{Ti, Zr, Hf}$ ;  $n = 7, 6, 5, 4$ ) were predicted using density functional theory. Analogous  $M(\text{CO})_n$  structures were found for all three metals. The global minima for the 18-electron  $M(\text{CO})_7$  molecules are all singlet  $C_{3v}$  capped octahedra. The global minima for the 16-electron  $M(\text{CO})_6$  species are triplet  $M(\text{CO})_6$  structures distorted from  $O_h$  symmetry to  $D_{3d}$  symmetry. However, the corresponding singlet  $M(\text{CO})_6$  structures lie within 5 kcal/mol of the triplet global minima. The global minima for  $M(\text{CO})_n$  ( $n = 5, 4$ ) are triplet structures derived from the  $D_{3d}$  distorted octahedral structures of  $M(\text{CO})_6$  by removal of one or two CO groups, respectively. Quintet  $D_{3h}$  trigonal bipyramidal structures for  $M(\text{CO})_5$  and singlet  $T_d$  tetrahedral structures for  $M(\text{CO})_4$  are also found, as well as higher energy structures for  $M(\text{CO})_6$  and  $M(\text{CO})_7$  containing a unique CO group bonded to the metal atom through both M–C and M–O bonds. The dissociation energies  $M(\text{CO})_7 \rightarrow M(\text{CO})_6 + \text{CO}$  are substantial, indicating no fundamental problem in bonding seven CO groups to a single metal atom.

### 1. Introduction

Coordination-saturated transition metal–carbonyls, which are among the most fundamental building blocks in inorganic and organometallic chemistry, have been the focus of extensive and continuous study since the early twentieth century.<sup>1</sup> Most of the stable binary metal–carbonyls satisfy a common principle, the so-called 18-electron rule, which is rationalized as a consequence of filling each of the nine valence orbitals of the transition metal  $sp^3d^5$  manifold with electron pairs so that the metal atom has the same electronic configuration as that of the next noble gas.<sup>2,3</sup> In this connection the homoleptic carbonyl complexes of first row metal elements with 18-electron configurations, such as  $\text{Ni}(\text{CO})_4$ ,  $\text{Fe}(\text{CO})_5$ , and  $\text{Cr}(\text{CO})_6$ , have been studied thoroughly. Extending the 18-electron rule to titanium suggests  $\text{Ti}(\text{CO})_7$  as a stable, or at least detectable, species.

The first experimental evidence for a binary titanium carbonyl was obtained in 1977 by matrix isolation spectroscopy.<sup>4</sup> Thus Busby, Klotzbücher, and Ozin (BKO)<sup>4</sup> reported the reaction of

titanium atoms with carbon monoxide at temperatures around 20 K in inert matrices to give a titanium carbonyl derivative characterized by two  $\nu(\text{CO})$  frequencies of  $1947 \pm 3$  and  $1985 \pm 3 \text{ cm}^{-1}$ . They formulated this titanium carbonyl derivative as the 16-electron neutral  $\text{Ti}(\text{CO})_6$  rather than the 18-electron  $\text{Ti}(\text{CO})_7$  based largely on this infrared spectroscopic evidence as well as an analysis of the electronic spectra using crystal field theory.<sup>5</sup>

The Ti/CO system was subsequently investigated in detail by Andrews and his group<sup>6</sup> using the reactions of pulsed laser ablated titanium atoms with carbon monoxide in low-temperature noble gas matrices. Chertihin and Andrews<sup>7</sup> suggested that the  $\nu(\text{CO})$  frequencies  $1947 \pm 3 \text{ cm}^{-1}$  assigned by BKO<sup>4</sup> to  $\text{Ti}(\text{CO})_6$  could indeed be  $\text{Ti}(\text{CO})_6$ . However, they assigned the  $1985 \pm 3 \text{ cm}^{-1}$   $\nu(\text{CO})$  frequency, also attributed by BKO to  $\text{Ti}(\text{CO})_6$ , instead to a peroxide  $\text{O}_2\text{Ti}(\text{CO})_4$ . Subsequent work by Zhou and Andrews,<sup>8</sup> operating at standard titanium atom fluxes in highly diluted neon matrices, led to complicated infrared  $\nu(\text{CO})$  spectra containing bands assigned to all of the titanium carbonyls  $\text{Ti}(\text{CO})_n$  ( $n = 2-6$ ) as well as the corresponding monoanions.

None of these matrix isolation studies led to any  $\nu(\text{CO})$  frequencies assigned to the heptacarbonyl  $\text{Ti}(\text{CO})_7$ , despite

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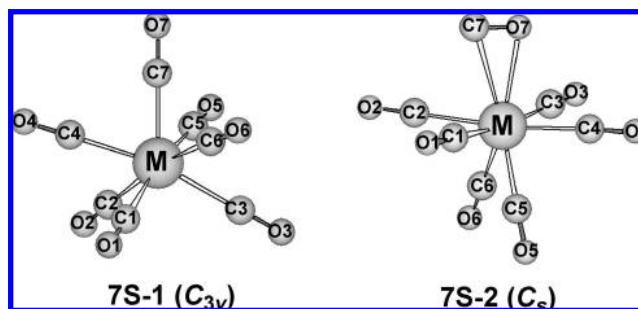
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its 18-electron configuration. The first report of a seven-coordinate homoleptic titanium heptacarbonyl was that of Meyer and Armentrout<sup>9</sup> for the radical cation  $\text{Ti}(\text{CO})_7^+$ , encountered during their study on the bond dissociation energies of  $\text{Ti}(\text{CO})_n$  ( $n = 1-7$ ) using guided ion beam mass spectrometry. However, the relatively weak bond energy of 12 kcal/mol for the 17-electron  $\text{Ti}(\text{CO})_7^+$  suggests that this cation is relatively less stable. Stable seven-coordinate derivatives of  $\text{Ti}(\text{CO})_7$  have been synthesized<sup>10</sup> in which two to four CO groups are replaced by highly basic chelating phosphines including  $(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)\text{Ti}(\text{CO})_5$  and  $[\text{MeC}(\text{CH}_2\text{PMe}_2)_3]\text{Ti}(\text{CO})_4$ . In addition the seven-coordinate titanium carbonyl anions  $[\text{R}_3\text{SnTi}(\text{CO})_6]^-$  ( $\text{R} = \text{Ph}$ )<sup>11</sup> and  $[\text{R}_3\text{PAu} \rightarrow \text{Ti}(\text{CO})_6]^-$  ( $\text{R} = \text{Et}$ )<sup>12</sup> have been synthesized and structurally characterized. These observations suggest that there might not be anything inherently unstable about seven CO or similar groups around a titanium atom.

Reports of homoleptic zirconium and hafnium carbonyls  $\text{M}(\text{CO})_n$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) are limited to a paper by Zhou and Andrews,<sup>13</sup> who have found species up to the tetracarbonyls  $\text{M}(\text{CO})_4$  from the co-condensation of laser ablated metal atoms with carbon monoxide in low temperature neon matrices.

The titanium carbonyl dianion  $\text{Ti}(\text{CO})_6^{2-}$  is an 18-electron complex isoelectronic with the stable species  $\text{V}(\text{CO})_6^-$  and  $\text{Cr}(\text{CO})_6$ . Salts of  $\text{Ti}(\text{CO})_6^{2-}$  with suitable counterions, first prepared by Ellis and co-workers in 1988,<sup>14</sup> are stable in accord with its favorable electronic configuration and octahedral metal coordination. However, because of the low formal oxidation state of  $-2$  for the central titanium atom, such  $\text{Ti}(\text{CO})_6^{2-}$  salts are strong nucleophiles and highly air-sensitive despite their favorable 18-electron metal configuration.

A comparison of the zerovalent bis(arene) complexes of titanium and zirconium suggests that there might be significant differences between the homoleptic zerovalent metal-carbonyl complexes  $\text{M}(\text{CO})_n$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ) of Ti and its heavier congeners zirconium and hafnium. Thus for titanium the 16-electron zerovalent bis(arene) sandwich compounds  $(\eta^6\text{-arene})_2\text{Ti}$  are an isolable, albeit very air-sensitive, species obtained from reactions of titanium vapor with various arenes.<sup>15</sup> However, the corresponding 16-electron bis(arene)zirconium derivatives  $(\eta^6\text{-arene})_2\text{Zr}$  do not appear at present to be isolable from analogous reactions. Instead, 18-electron complexes of the type  $(\eta^6\text{-arene})_2\text{Zr} \cdot \text{PMe}_3$  can be isolated from such Zr vapor/arene reactions by addition of trimethylphosphine.<sup>16</sup> Extrapolation of these observations from bis(arene)metal chemistry to homoleptic metal-carbonyl chemistry would seem to suggest significant differences between  $\text{Ti}(\text{CO})_n$  and  $\text{Zr}(\text{CO})_n$  derivatives. Thus the 18-electron seven-coordinate  $\text{Zr}(\text{CO})_7$  might be the most stable accessible zirconium carbonyl whereas the analogous  $\text{Ti}(\text{CO})_7$  would be unstable with respect to CO loss to give the 16-



**Figure 1.** Two structures found for  $\text{M}(\text{CO})_7$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ). The vertical  $\text{M}-\text{C}_7-\text{O}_7$  in **7S-1** is on the  $\text{C}_3$  axis, and the unique CO group for **7S-2** is on the symmetry plane.

electron  $\text{Ti}(\text{CO})_6$ . This would, of course, be consistent with the experimental reports of  $\text{Ti}(\text{CO})_6$  from the Ti/CO matrix reactions cited above but not the apparent absence of  $\text{Ti}(\text{CO})_7$  in these reaction mixtures, even at low temperatures. Experimental data on homoleptic zirconium and hafnium carbonyl derivatives appear to be limited to syntheses of salts of the 18-electron dianions<sup>17,18</sup>  $\text{M}(\text{CO})_6^{2-}$  ( $\text{M} = \text{Zr}, \text{Hf}$ ). No experimental information on neutral  $\text{Zr}(\text{CO})_6$ , even in low temperature matrices, appears to be present in the literature.

The present paper reports density functional theory (DFT) studies on neutral  $\text{M}(\text{CO})_n$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}; n = 7, 6, 5, 4$ ) species. These studies suggest that the 18-electron species  $\text{M}(\text{CO})_7$ , even  $\text{Ti}(\text{CO})_7$ , are reasonable molecules despite the metal coordination numbers of seven. Thus the energies of CO loss from  $\text{M}(\text{CO})_7$  to  $\text{M}(\text{CO})_6$  for all three metals are not found to be unusually low but instead are comparable to the energies of CO loss from  $\text{M}(\text{CO})_6$  and  $\text{M}(\text{CO})_5$ . In addition, the chemistry of the zirconium and hafnium derivatives  $\text{M}(\text{CO})_n$  is predicted to be very similar to that of the corresponding titanium derivatives  $\text{Ti}(\text{CO})_n$ .

## 2. Theoretical Methods

All-electron double- $\zeta$  plus polarization (DZP) basis sets are used for carbon and oxygen atoms, which are formed by adding one set of pure spherical harmonic d functions with orbital exponents  $\alpha_d(\text{C}) = 0.75$  and  $\alpha_d(\text{O}) = 0.85$  to the standard Huzinaga-Dunning contracted double- $\zeta$  sets and are designated  $(9s5p1d/4s2p1d)$ .<sup>19,20</sup> For the first-row transition metal titanium, the all-electron DZP basis set was the Wachters primitive set augmented by two sets of p functions and a set of d functions, contracted following Hood, Pitzer, and Schaefer, and designated as  $(14s11p6d/10s8p3d)$ .<sup>21,22</sup> For the second- and third-row transition metals zirconium and hafnium, effective core potentials (ECPs) were used. In the present research we adopted the Stuttgart/Dresden double- $\zeta$  (SDD) ECP basis sets.<sup>23</sup> In these basis sets the core-electrons (28 for Zr and 60 for Hf) for the transition metal atoms are replaced by effective core potentials (ECP), which include relativistic effects known to be important for the heavy transition metal atoms. For the valence electrons (12 for both Zr and Hf) the SDD ECP basis sets can be designated  $(8s7p6d/6s5p3d)$ . Calculations using this ECP basis set were also performed for the titanium carbonyls and gave results similar to

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Table 1. Geometric Parameters for M(CO)<sub>7</sub>

species	bonds	BP86			MPW1PW91			B3LYP		
		Ti	Zr	Hf	Ti	Zr	Hf	Ti	Zr	Hf
7S-1 (C <sub>3v</sub> )	M–C <sub>1</sub> , M–C <sub>2</sub> , M–C <sub>3</sub>	2.121	2.303	2.290	2.076	2.303	2.288	2.150	2.278	2.269
	M–C <sub>4</sub> , M–C <sub>5</sub> , M–C <sub>6</sub>	2.081	2.259	2.254	2.120	2.254	2.248	2.106	2.323	2.306
	M–C <sub>7</sub>	2.046	2.209	2.211	2.043	2.206	2.206	2.076	2.236	2.235
	C <sub>1</sub> –O <sub>1</sub> , C <sub>2</sub> –O <sub>2</sub> , C <sub>3</sub> –O <sub>3</sub>	1.166	1.166	1.167	1.153	1.147	1.148	1.152	1.156	1.157
	C <sub>4</sub> –O <sub>4</sub> , C <sub>5</sub> –O <sub>5</sub> , C <sub>6</sub> –O <sub>6</sub>	1.171	1.170	1.171	1.148	1.152	1.152	1.157	1.152	1.153
	C <sub>7</sub> –O <sub>7</sub>	1.174	1.172	1.172	1.156	1.154	1.154	1.159	1.158	1.159
7S-2 (C <sub>s</sub> )	M–C <sub>1</sub>	2.100	2.270	2.260	2.094	2.264	2.253	2.121	2.286	2.272
	M–C <sub>3</sub>	2.112	2.282	2.271	2.109	2.279	2.269	2.133	2.300	2.287
	M–C <sub>5</sub>	2.037	2.202	2.204	2.034	2.198	2.199	2.064	2.225	2.224
	M–C <sub>7</sub>	2.640	2.708	2.678	2.684	2.725	2.688	2.818	2.783	2.743
	M–O <sub>7</sub>	2.480	2.546	2.509	2.495	2.543	2.501	2.583	2.577	2.534
	C <sub>1</sub> –O <sub>1</sub> , C <sub>2</sub> –O <sub>2</sub>	1.169	1.168	1.169	1.151	1.150	1.151	1.156	1.155	1.156
	C <sub>3</sub> –O <sub>3</sub> , C <sub>4</sub> –O <sub>4</sub>	1.168	1.168	1.168	1.149	1.149	1.150	1.154	1.154	1.155
	C <sub>5</sub> –O <sub>5</sub> , C <sub>6</sub> –O <sub>6</sub>	1.175	1.173	1.173	1.157	1.155	1.155	1.161	1.159	1.159
	C <sub>7</sub> –O <sub>7</sub>	1.176	1.181	1.185	1.155	1.161	1.165	1.156	1.165	1.168

those using the all-electron DZP basis set noted above (see Supporting Information).

Density functional theory (DFT) appears to be a powerful and effective computational tool to study organotransition metal chemistry.<sup>24–32</sup> Three DFT methods were used for this work. The first DFT method was BP86, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86).<sup>33,34</sup> The second functional was B3LYP, which is the hybrid HF/DFT functional using the combination of the three-parameter Becke functional (B3) with the Lee–Yang–Parr (LYP) generalized gradient correlation functional.<sup>35,36</sup> The third DFT method was a new generation functional MPW1PW91, which is a combination of the modified Perdew–Wang exchange functional with Perdew–Wang's 91 gradient-correlation functional.<sup>37</sup> This MPW1PW91 functional has been shown to be better than the B3LYP functional for the second- and third-row transition metal compounds.<sup>38,39</sup> Although all of the results by different methods are shown in the tables, unless specifically noted, only the BP86 results (geometries, energies, and vibrational frequencies) are discussed in the text. All of the computations were carried out with the Gaussian 03 program.<sup>40</sup>

### 3. Results and Discussion

**3.1. Structures. 3.1.1. M(CO)<sub>7</sub>.** The conceivable structures for seven-coordinate M(CO)<sub>7</sub> include the pentagonal bipyramid (*D*<sub>5h</sub>), the capped octahedron (*C*<sub>3v</sub>), and the face-capped trigonal prism (*C*<sub>2v</sub>). However, the *D*<sub>5h</sub> and *C*<sub>2v</sub> structures are found to be saddle points with imaginary vibrational frequencies. By

following the corresponding normal modes for all three metals, both structures collapse to the *C*<sub>3v</sub> face-capped octahedron **7S-1** (Figure 1). Structure **7S-1** is thus predicted by all three DFT methods to be the global minimum with the singlet electron state, and the transition metal atoms (Ti, Zr, and Hf) satisfy the 18-electron configuration. The geometric parameters of M(CO)<sub>7</sub> (M = Ti, Zr, and Hf) are reported in Table 1. The axial M–C bond distance predicted by BP86 for Ti(CO)<sub>7</sub> is 2.121 Å, and those for Zr(CO)<sub>7</sub> and Hf(CO)<sub>7</sub> are 2.303 and 2.290 Å, respectively. The other M–C distances are shorter by ~0.05 Å. All C–O distances are within 0.02 Å of ~1.16 Å (Table 1).

For M(CO)<sub>7</sub> (M = Ti, Zr, and Hf) compounds, there is an unexpected singlet minimum **7S-2** with *C*<sub>s</sub> symmetry and a special eight-coordinate geometry, with one of the CO groups bonded to the metal atom through both of its carbon and oxygen atoms (Figure 1). For this unique carbonyl group in **7S-2** (Figure 1: M = Ti, Zr, Hf) the M–C distances are all ~2.7 Å, and the M–O distances are all ~2.5 Å (BP86, Table 1). The shorter M–O distances relative to the M–C distances for this unique CO group in **7S-2** are consistent with the oxophilicity of the group 4 metals Ti, Zr, and Hf. For all three metals all three DFT methods used for each metal predict the M(CO)<sub>7</sub> structures **7S-2** to lie 17–22 kcal/mol above the global minima **7S-1** (Table 2).

**3.1.2. M(CO)<sub>6</sub>.** DFT optimization of either triplet or singlet six-coordinated M(CO)<sub>6</sub> leads to *D*<sub>3d</sub> trigonal antiprismatic structures (**6T** and **6S-1**, respectively). These structures are distorted from ideal octahedral symmetry as expected from the second-order Jahn–Teller effect for a strong-field d<sup>4</sup> metal complex in the t<sub>2g</sub> orbital set (Figure 2). The singlet *D*<sub>3d</sub> structure **6S-1** is a local minimum. The M–C distances for the singlet **6S-1** are 2.106 Å for Ti(CO)<sub>6</sub>, those for Zr(CO)<sub>6</sub> are 0.1 Å longer (2.273 Å), and those for Hf(CO)<sub>6</sub> are 2.261 Å, which is slightly shorter than that in Zr(CO)<sub>6</sub> (Table 3).

The less distorted triplet structure **6T** is the global minimum, lying 2.4, 0.7, and 1.3 kcal/mol for Ti(CO)<sub>6</sub>, Zr(CO)<sub>6</sub>, and Hf(CO)<sub>6</sub>, respectively, energetically below the singlet structure **6S-1** (Table 4). The spin contamination for **6T** is negligible ( $\langle S^2 \rangle < 2.01$ , see Table 4). The M–C distances for **6T** are about 0.01 Å longer than their corresponding M–C distances for **6S-1**. The C–O distances for all compounds are within 0.03 Å of 1.16 Å (Table 3).

Similar to M(CO)<sub>7</sub>, there is a special seven-coordinate structure for M(CO)<sub>6</sub>, namely **6S-2**, with a unique CO group

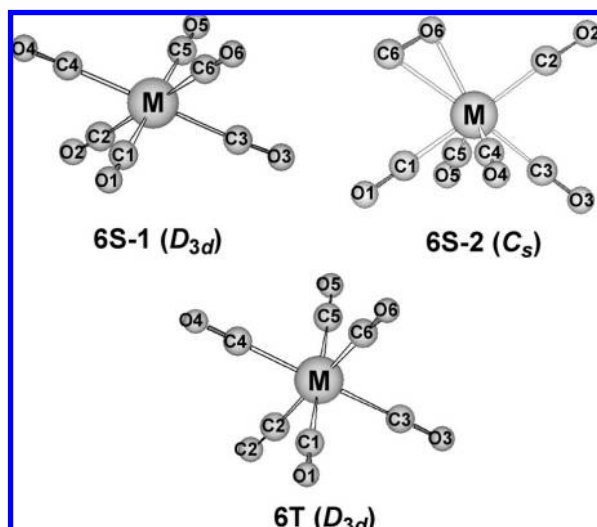
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**Table 2.** Total Energies ( $E$  in hartrees), Relative Energies ( $\Delta E$  in kcal/mol), the Number of Imaginary Vibrational Frequencies (Nimag), and the Lowest Vibrational Frequency ( $\nu_1$ , in  $\text{cm}^{-1}$ ) for  $\text{M}(\text{CO})_7$ 

		Ti		Zr		Hf	
		7S-1( $C_{3v}$ )	7S-2( $C_s$ )	7S-1( $C_{3v}$ )	7S-2( $C_s$ )	7S-1( $C_{3v}$ )	7S-2( $C_s$ )
BP86	state	$^1A_1$	$^1A'$	$^1A_1$	$^1A'$	$^1A_1$	$^1A'$
	$E$	-1643.143 68	-1643.109 79	-840.665 98	-840.637 21	-841.640 58	-841.609 39
	$\Delta E$	0.0	21.3	0.0	18.0	0.0	19.6
	Nimag	0	0	0	0	0	0
	$\nu_1$	38	25	43	43	43	37
MPW1PW91	state	$^1A_1$	$^1A'$	$^1A_1$	$^1A'$	$^1A_1$	$^1A'$
	$E$	-1642.792 97	-1642.759 79	-840.351 38	-840.322 94	-841.309 83	-841.278 92
	$\Delta E$	0.0	20.8	0.0	17.8	0.0	19.4
	Nimag	0	0	0	0	0	0
	$\nu_1$	36	27	44	47	44	47
B3LYP	state	$^1A_1$	$^1A'$	$^1A_1$	$^1A'$	$^1A_1$	$^1A'$
	$E$	-1642.984 70	-1642.954 20	-840.566 35	-840.538 87	-841.524 74	-841.494 71
	$\Delta E$	0.0	19.1	0.0	17.2	0.0	18.8
	Nimag	0	1	0	0	0	0
	$\nu_1$	35	24i	41	41	40	37

**Table 3.** Geometric Parameters for  $\text{M}(\text{CO})_6$ 

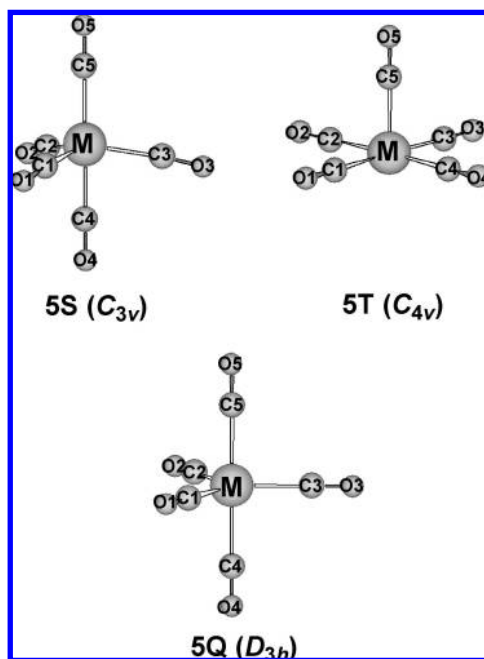
species	bonds	BP86			MPW1PW91			B3LYP		
		Ti	Zr	Hf	Ti	Zr	Hf	Ti	Zr	Hf
<b>6S-1</b> ( $D_{3d}$ )	M–C <sub>1</sub> , M–C <sub>2</sub> , M–C <sub>3</sub> , M–C <sub>4</sub> , M–C <sub>5</sub> , M–C <sub>6</sub>	2.106	2.273	2.261	2.103	2.269	2.257	2.127	2.289	2.274
	C <sub>1</sub> –O <sub>1</sub> , C <sub>2</sub> –O <sub>2</sub> , C <sub>3</sub> –O <sub>3</sub> , C <sub>4</sub> –O <sub>4</sub> , C <sub>5</sub> –O <sub>5</sub> , C <sub>6</sub> –O <sub>6</sub>	1.170	1.170	1.171	1.151	1.151	1.152	1.156	1.156	1.157
<b>6S-2</b> ( $C_1$ )	M–C <sub>1</sub>	2.049	2.227	2.219	2.035	2.217	2.206	2.065	2.240	2.228
	M–C <sub>2</sub>	2.130	2.296	2.278	2.129	2.301	2.284	2.142	2.314	2.293
	M–C <sub>3</sub>	2.042	2.188	2.197	2.041	2.179	2.186	2.076	2.210	2.216
	M–C <sub>4</sub>	2.043	2.180	2.182	2.050	2.177	2.176	2.089	2.206	2.205
	M–C <sub>5</sub>	2.043	2.199	2.198	2.050	2.198	2.196	2.089	2.226	2.224
	M–C <sub>6</sub>	2.465	2.626	2.578	2.464	2.639	2.586	2.500	2.670	2.613
	M–O <sub>6</sub>	2.234	2.432	2.372	2.227	2.437	2.377	2.248	2.444	2.380
	C <sub>1</sub> –O <sub>1</sub>	1.175	1.172	1.173	1.158	1.154	1.156	1.161	1.159	1.160
	C <sub>2</sub> –O <sub>2</sub>	1.167	1.167	1.168	1.148	1.148	1.148	1.153	1.153	1.154
	C <sub>3</sub> –O <sub>3</sub>	1.176	1.175	1.175	1.157	1.158	1.158	1.160	1.161	1.161
	C <sub>4</sub> –O <sub>4</sub>	1.173	1.174	1.174	1.153	1.156	1.156	1.156	1.160	1.160
	C <sub>5</sub> –O <sub>5</sub>	1.173	1.173	1.174	1.153	1.155	1.155	1.156	1.159	1.159
C <sub>6</sub> –O <sub>6</sub>	1.196	1.192	1.200	1.175	1.171	1.178	1.179	1.176	1.184	
<b>6T</b> ( $D_{3d}$ )	M–C <sub>1</sub> , M–C <sub>2</sub> , M–C <sub>3</sub> , M–C <sub>4</sub> , M–C <sub>5</sub> , M–C <sub>6</sub>	2.117	2.283	2.269	2.114	2.280	2.264	2.136	2.297	2.280
	C <sub>1</sub> –O <sub>1</sub> , C <sub>2</sub> –O <sub>2</sub> , C <sub>3</sub> –O <sub>3</sub> , C <sub>4</sub> –O <sub>4</sub> , C <sub>5</sub> –O <sub>5</sub> , C <sub>6</sub> –O <sub>6</sub>	1.168	1.169	1.170	1.150	1.150	1.151	1.155	1.155	1.156

**Figure 2.** Three structures found for  $\text{M}(\text{CO})_6$  ( $M = \text{Ti}, \text{Zr}$  and  $\text{Hf}$ ). In the  $C_s$  structure **6S-2** the symmetry plane contains the carbonyl groups C<sub>1</sub>–O<sub>1</sub>, C<sub>2</sub>–O<sub>2</sub>, C<sub>3</sub>–O<sub>3</sub>, and C<sub>6</sub>–O<sub>6</sub> as well as the metal atom M.

bonded to the metal atom through oxygen as well as carbon. This structure is a genuine minimum for all the three transition metals (Ti, Zr, and Hf) and lies above the corresponding structures **6S-1** by 8 to 15 kcal/mol or **6T** by 10 to 20 kcal/mol depending on the metal and DFT method. For  $\text{Ti}(\text{CO})_6$ , the symmetry of **6S-2** is  $C_s$  with a coplanar  $\text{MC}_4\text{O}$  unit containing the unique CO group. For  $\text{Zr}(\text{CO})_6$  and  $\text{Hf}(\text{CO})_6$ , the unique CO group no longer lies in an  $\text{MC}_4\text{O}$  plane, thereby leading to structures with no symmetry. The terminal M–C distances for  $\text{Ti}(\text{CO})_6$  are about 2.05 Å, except for the Ti–C distance of 2.130 Å *trans* to the unique CO group. This indicates a strong *trans* effect for an  $\eta^2$ -CO group. For  $\text{Zr}(\text{CO})_6$  the Zr–C distances are 0.14–0.16 Å longer while the conventional Hf–C distances for  $\text{Hf}(\text{CO})_6$  are almost the same as the Zr–C distances in  $\text{Zr}(\text{CO})_6$ . The M–C distance to the unique CO group is significantly longer, i.e., 2.47 Å for Ti, 2.63 Å for Zr, and 2.58 Å for Hf (Table 3). The M–O distance is shorter than the corresponding M–C distance, and it is 2.23 Å for Ti, 2.43 Å for Zr, and 2.37 Å for Hf again in accord with the oxophilicities of the early transition metals. If this unique CO group is considered to be a formal four-electron donor similar to the related alkyne

**Table 4.** Total Energies ( $E$  in hartrees), Relative Energies ( $\Delta E$  in kcal/mol), the Number of Imaginary Vibrational Frequencies (Nimag), and the Lowest Vibrational Frequency ( $\nu_1$ , in  $\text{cm}^{-1}$ ) for  $\text{M}(\text{CO})_6$ 

state	Ti			Zr			Hf			
	6S-1 ( $D_{3d}$ )	6S-2 ( $C_s$ )	6T ( $D_{3d}$ )	6S-1 ( $D_{3d}$ )	6S-2 ( $C_1$ )	6T ( $D_{3d}$ )	6S-1 ( $D_{3d}$ )	6S-2 ( $C_1$ )	6T ( $D_{3d}$ )	
	$^1A_{1g}$	$^1A'$	$^3A_{1g}$	$^1A_{1g}$	$^1A$	$^3A_{1g}$	$^1A_{1g}$	$^1A$	$^3A_{1g}$	
BP86	$E$	-1529.762 21	-1529.743 79	-1529.766 08	-727.280 90	-727.266 84	-727.28 199	-728.25 454	-728.236 64	-728.256 56
	$\Delta E$	2.43	14.0	0.0	0.7	9.5	0.0	1.3	12.5	0.0
	Nimag	0	0	0	0	0	1	0	0	0
	$\nu_1$	41	12	13	37	37	8i	35	33	5
	$\langle S^2 \rangle$			2.0036			2.0025			2.0024
MPW1PW91	$E$	-1529.450 47	-1529.428 24	-1529.457 63	-727.002 45	-726.986 05	-727.005 53	-727.959 31	-727.939 61	-727.963 22
	$\Delta E$	4.5	18.4	0.0	1.9	12.2	0.0	2.4	14.8	0.0
	Nimag	0	1	0	0	0	0	0	0	0
	$\nu_1$	49	11i	20	47	41	9	43	39	14
	$\langle S^2 \rangle$			2.0078			2.0048			2.0048
B3LYP	$E$	-1529.617 27	-1529.592 80	-1529.624 08	-727.189 67	-727.170 84	-727.192 98	-728.146 79	-728.124 45	-728.150 59
	$\Delta E$	4.3	19.6	0.0	2.1	13.9	0.0	2.4	16.4	0.0
	Nimag	0	0	0	0	0	0	0	0	0
	$\nu_1$	46	20	26	45	38	17	44	34	18
	$\langle S^2 \rangle$			2.0057			2.0029			2.0029

**Figure 3.** Three structures found for  $\text{M}(\text{CO})_5$  ( $M = \text{Ti}, \text{Zr}$  and  $\text{Hf}$ ). The vertical  $\text{C}_4\text{-O}_4\text{-M-C}_5\text{-O}_5$  in **5S** is on the  $\text{C}_3$  axis. The vertical  $\text{M-C}_5\text{-O}_5$  in **5T** is on the  $\text{C}_4$  axis. The vertical  $\text{C}_4\text{-O}_4\text{-M-C}_5\text{-O}_5$  in **5Q** is on the  $\text{C}_3$  axis.

ligands in certain alkyne complexes<sup>41</sup> such as  $(\text{RC}\equiv\text{CR})_3\text{W}(\text{CO})$ , then the group 4 metal atoms in **6S-2** have the favored 18-electron configurations.

**3.1.3.  $\text{M}(\text{CO})_5$ .** Structures of  $\text{M}(\text{CO})_5$  with 14-electron metal configurations are found with various multiplicities ranging from singlet to quintet (Figure 3, Tables 5 and 6). For both  $\text{Ti}(\text{CO})_5$  and  $\text{Hf}(\text{CO})_5$  the  $\text{C}_{4v}$  triplet square pyramidal structure **5T** (Figure 3) has the lowest energy (Table 6). For  $\text{Zr}(\text{CO})_5$  BP86 predicts that the singlet structure **5S** has a lower energy than **5T** by 0.9 kcal/mol. In some cases, **5T** is found to have a very small imaginary vibrational frequency (less than  $40i \text{ cm}^{-1}$ ),

which may come from numerical integration errors.<sup>42</sup> It is reasonable to consider the  $\text{C}_{4v}$  structure **5T** to be the global minimum for all three transition metals. Table 5 shows that the  $\text{M-C}$  distances (axial and equatorial) in **5T** are 2.096 and 2.085 Å for  $\text{Ti}(\text{CO})_5$ . The  $\text{M-C}$  distances in  $\text{Zr}(\text{CO})_5$  (2.258 and 2.219 Å) are  $\sim 0.15$  Å longer, and those in  $\text{Hf}(\text{CO})_5$  (2.243 and 2.201 Å) are slightly shorter than those for  $\text{Zr}(\text{CO})_5$  (Table 5). The singlet  $\text{C}_{3v}$  structure **5S** has a distorted trigonal bipyramidal configuration and lies above the global minimum **5T** by only 4.0 kcal/mol for  $\text{Ti}(\text{CO})_5$ . The energy differences between structures **5S** and **5T** for  $\text{Zr}(\text{CO})_5$  and  $\text{Hf}(\text{CO})_5$  are less than 1 kcal/mol.

The quintet structure **5Q** with ideal trigonal bipyramidal ( $\text{D}_{3h}$ ) symmetry lies above the global minimum by about 10 to 15 kcal/mol. Table 5 shows that the  $\text{M-C}$  ( $M = \text{Ti}, \text{Zr}, \text{Hf}$ ) distances in **5Q** are close to those in **5T** and **5S**. The quintet spin multiplicity for the 14-electron complexes  $\text{M}(\text{CO})_5$  (**5Q**) can arise from each of the four orbitals of the  $\text{sp}^3\text{d}^5$  valence orbital manifold of the central metal atom  $M$  not involved in the  $\text{M-CO}$   $\sigma$ -bonding to the five CO groups being occupied by a single electron rather than an electron pair.

**3.1.4.  $\text{M}(\text{CO})_4$ .** Similar to  $\text{M}(\text{CO})_5$ , the isomers of  $\text{M}(\text{CO})_4$  are also found with various multiplicities ranging from singlet to quintet (Figure 4, Tables 7 and 8). The global minima are the  $\text{C}_{2v}$  triplet structures **4T**, which can be derived by removal of two *cis*-CO groups from the model octahedral  $\text{M}(\text{CO})_6$ . The  $\text{M-C}$  distances in  $\text{Ti}(\text{CO})_4$  are 2.08 and 2.02 Å, and those in  $\text{Zr}(\text{CO})_4$  and  $\text{Hf}(\text{CO})_4$  are 0.12 to 0.16 Å longer (Table 7).

The singlet **4S** ( $T_d$  symmetry, like  $\text{Cr}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_4$ <sup>43,44</sup>) and quintet **4Q** ( $\text{C}_{3v}$  symmetry, an axial CO group removed from a trigonal bipyramid) structures for  $\text{M}(\text{CO})_4$  are also predicted to be genuine minima, but they lie in energy above the triplet global minimum by 3 to 20 kcal/mol (Table 8). For  $\text{Ti}(\text{CO})_4$ , the quintet structure **4Q** has lower energy than the singlet **4S**, while, for  $\text{Zr}(\text{CO})_4$  and  $\text{Hf}(\text{CO})_4$ , the relative energies for **4Q** and **4S** are dependent on the DFT method used for the calculation (Table 8).

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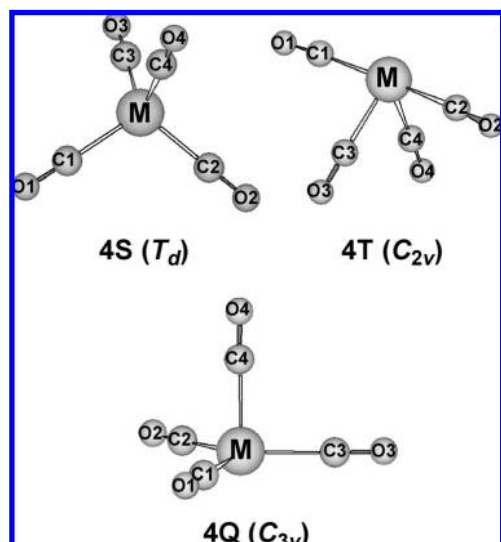
**Table 5.** Geometric Parameters for  $M(\text{CO})_5$ 

species	bonds	BP86			MPW1PW91			B3LYP		
		Ti	Zr	Hf	Ti	Zr	Hf	Ti	Zr	Hf
<b>5S</b> ( $C_{3v}$ )	M–C <sub>1</sub> , M–C <sub>2</sub> , M–C <sub>3</sub>	2.064	2.202	2.196	2.077	2.210	2.202	2.104	2.234	2.224
	M–C <sub>4</sub>	2.021	2.192	2.194	2.006	2.175	2.174	2.040	2.206	2.202
	M–C <sub>5</sub>	2.152	2.314	2.279	2.137	2.314	2.276	2.138	2.311	2.275
	C <sub>1</sub> –O <sub>1</sub> , C <sub>2</sub> –O <sub>2</sub> , C <sub>3</sub> –O <sub>3</sub>	1.173	1.175	1.176	1.153	1.155	1.156	1.157	1.159	1.160
	C <sub>4</sub> –O <sub>4</sub>	1.181	1.178	1.179	1.164	1.162	1.162	1.167	1.165	1.166
<b>5T</b> ( $C_{4v}$ )	M–C <sub>1</sub> , M–C <sub>2</sub> , M–C <sub>3</sub> , M–C <sub>4</sub>	2.096	2.258	2.243	2.092	2.254	2.238	2.114	2.271	2.253
	M–C <sub>5</sub>	2.085	2.219	2.201	2.088	2.216	2.195	2.110	2.232	2.208
	C <sub>1</sub> –O <sub>1</sub> , C <sub>2</sub> –O <sub>2</sub> , C <sub>3</sub> –O <sub>3</sub> , C <sub>4</sub> –O <sub>4</sub>	1.172	1.172	1.174	1.153	1.153	1.154	1.157	1.158	1.160
	C <sub>5</sub> –O <sub>5</sub>	1.169	1.172	1.174	1.151	1.154	1.156	1.155	1.159	1.161
	<b>5Q</b> ( $D_{3h}$ )	M–C <sub>1</sub> , M–C <sub>2</sub> , M–C <sub>3</sub>	2.105	2.252	2.233	2.102	2.252	2.231	2.119	2.264
M–C <sub>4</sub> , M–C <sub>5</sub>		2.143	2.304	2.284	2.143	2.302	2.279	2.163	2.317	2.292
C <sub>1</sub> –O <sub>1</sub> , C <sub>2</sub> –O <sub>2</sub> , C <sub>3</sub> –O <sub>3</sub>		1.171	1.174	1.175	1.153	1.154	1.150	1.158	1.160	1.161
C <sub>4</sub> –O <sub>4</sub> , C <sub>5</sub> –O <sub>5</sub>		1.167	1.167	1.169	1.148	1.148	1.156	1.153	1.154	1.155

**Table 6.** Total Energies ( $E$  in hartrees), Relative Energies ( $\Delta E$  in kcal/mol), the Number of Imaginary Vibrational Frequencies (Nimag), and the Lowest Vibrational Frequency ( $\nu_1$ , in  $\text{cm}^{-1}$ ) for  $M(\text{CO})_5$ 

	state	Ti			Zr			Hf		
		<b>5S</b> ( $C_{3v}$ )	<b>5T</b> ( $C_{4v}$ )	<b>5Q</b> ( $D_{3h}$ )	<b>5S</b> ( $C_{3v}$ )	<b>5T</b> ( $C_{4v}$ )	<b>5Q</b> ( $D_{3h}$ )	<b>5S</b> ( $C_{3v}$ )	<b>5T</b> ( $C_{4v}$ )	<b>5Q</b> ( $D_{3h}$ )
		$^1A_1$	$^3A_1$	$^5A_1'$	$^1A_1$	$^3A_1$	$^5A_1'$	$^1A_1$	$^3A_1$	$^5A_1'$
BP86	$E$	-1416.386 21	-1416.392 56	-1416.376 91	-613.909 21	-613.907 81	-613.885 23	-614.878 08	-614.878 25	-614.859 25
	$\Delta E$	4.0	0.0	9.8	-0.9	0.0	14.1	0.1	0.0	11.9
	Nimag	0	2	0	0	2	0	0	2	0
	$\nu_1$	49	23i	28	46	37i	20	48	28i	24
MPW1PW91	$E$	-1416.105 739	-1416.120 045	-1416.110 98	-613.660 77	-613.666 71	-613.649 41	-614.613 14	-614.620 36	-614.607 53
	$\Delta E$	9.0	0.0	5.7	3.7	0.0	11.0	4.50	0.0	8.0
	Nimag	0	0	0	0	2	0	0	0	0
	$\nu_1$	51	26	28	48	14i	22	50	14	24
B3LYP	$E$	-1416.242 94	-1416.2548	-1416.2435	-613.817 34	-613.821 59	-613.802 16	-614.769 90	-614.775 14	-614.759 62
	$\Delta E$	7.4	0.0	7.1	2.7	0.0	12.2	3.3	0.0	9.7
	Nimag	0	0	0	0	0	0	0	0	0
	$\nu_1$	49	34	28	49	19	23	52	28	24

The tetrahedral singlet  $M(\text{CO})_4$  isomers **4S** are the most symmetrical  $M(\text{CO})_n$  structures found in this work. They have a 12-electron configuration, which can be rationalized in terms of a filled six-orbital  $sd^5$  manifold with empty p orbitals. This

**Figure 4.** Three structures found for  $M(\text{CO})_4$  ( $M = \text{Ti}, \text{Zr}$  and  $\text{Hf}$ ). The vertical  $M\text{--}C_4\text{--}O_4$  in **4Q** is on the  $C_3$  axis.

electronic configuration may be considered to be a pseudorear gas electronic configuration, isoelectronic with atomic mercury.<sup>45</sup>

**3.2. Energetics.** A critical property in characterizing metal–carbonyl complexes is the bond dissociation energy (BDE). The sequential BDEs for  $M(\text{CO})_n$  ( $n = 5, 6, 7$ ) are predicted with the three DFT methods for the following reactions  $M(\text{CO})_n \rightarrow M(\text{CO})_{n-1} + \text{CO}$ .

The  $C_{3v}$  capped octahedral structures predicted for the 18-electron complexes  $M(\text{CO})_7$  **7S-1** (Figure 1) hint that loss of the face-capping CO group to give the distorted octahedral 16-electron complex  $M(\text{CO})_6$  **6S-1** or **6T** (Figure 2) might be unusually facile as indicated by low bond dissociation energies. However, our computed bond dissociation energies (Table 9) indicate that this is not the case. Thus the substantially large BDE of  $\text{Ti}(\text{CO})_7$  of 31.6 kcal/mol (BP86) is comparable to the BDEs<sup>46</sup> 27, 41, and 37 kcal/mol for  $\text{Ni}(\text{CO})_4$ ,  $\text{Fe}(\text{CO})_5$ , and  $\text{Cr}(\text{CO})_6$ , respectively. This indicates that the 18-electron configuration of  $M(\text{CO})_7$  ( $M = \text{Ti}, \text{Zr}, \text{Hf}$ ) overrides any energetic advantage of octahedral coordination in the 16-electron  $M(\text{CO})_6$ , e.g., from a more favorable orbital overlap. In other words, the “last” carbonyl capped to the  $D_{3d}$   $\text{Ti}(\text{CO})_6$  molecule along the 3-fold axis can form a strong bond with the metal

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**Table 7.** Geometric Parameters for  $M(\text{CO})_4$ 

species	bonds	BP86			MPW1PW91			B3LYP		
		Ti	Zr	Hf	Ti	Zr	Hf	Ti	Zr	Hf
<b>4S</b> ( $T_d$ )	M–C	2.073	2.201	2.187	2.082	2.208	2.191	2.098	2.223	2.204
	C–O	1.176	1.178	1.180	1.156	1.158	1.159	1.160	1.163	1.165
<b>4T</b> ( $C_{2v}$ )	M–C <sub>1</sub> , M–C <sub>2</sub>	2.085	2.241	2.223	2.082	2.239	2.219	2.102	2.254	2.233
	M–C <sub>3</sub> , M–C <sub>4</sub>	2.021	2.155	2.145	2.025	2.155	2.142	2.051	2.175	2.159
	C <sub>1</sub> –O <sub>1</sub> , C <sub>2</sub> –O <sub>2</sub>	1.175	1.176	1.177	1.155	1.156	1.157	1.160	1.161	1.163
	C <sub>3</sub> –O <sub>3</sub> , C <sub>4</sub> –O <sub>4</sub>	1.178	1.179	1.181	1.159	1.160	1.162	1.163	1.165	1.167
<b>4Q</b> ( $C_{3v}$ )	M–C <sub>1</sub> , M–C <sub>2</sub> , M–C <sub>3</sub>	2.103	2.242	2.221	2.103	2.244	2.221	2.118	2.256	2.231
	M–C <sub>4</sub>	2.077	2.203	2.183	2.083	2.202	2.178	2.100	2.214	2.188
	C <sub>1</sub> –O <sub>1</sub> , C <sub>2</sub> –O <sub>2</sub> , C <sub>3</sub> –O <sub>3</sub>	1.174	1.177	1.178	1.154	1.157	1.158	1.160	1.163	1.164
	C <sub>4</sub> –O <sub>4</sub>	1.172	1.174	1.176	1.152	1.155	1.158	1.157	1.161	1.164

**Table 8.** Total Energies ( $E$  in hartrees), Relative Energies ( $\Delta E$  in kcal/mol), the Number of Imaginary Vibrational Frequencies (Nimag), and the Lowest Vibrational Frequency ( $\nu_1$ , in  $\text{cm}^{-1}$ ) for  $M(\text{CO})_4$ 

state	Ti			Zr			Hf			
	<b>4S</b> ( $T_d$ )	<b>4T</b> ( $C_{2v}$ )	<b>4Q</b> ( $C_{3v}$ )	<b>4S</b> ( $T_d$ )	<b>4T</b> ( $C_{2v}$ )	<b>4Q</b> ( $C_{3v}$ )	<b>4S</b> ( $T_d$ )	<b>4T</b> ( $C_{2v}$ )	<b>4Q</b> ( $C_{3v}$ )	
	$^1A_1$	$^3A_2$	$^5A_1$	$^1A_1$	$^3A_2$	$^5A_1$	$^1A_1$	$^3A_2$	$^5A_1$	
BP86	$E$	–1302.991 47	–1303.014 46	–1303.001 39	–500.516 80	–500.530 19	–500.508 85	–501.482 79	–501.495 47	–501.477 96
	$\Delta E$	14.4	0.0	8.2	8.4	0.0	13.0	8.0	0.0	11.0
	Nimag	0	0	0	0	0	0	0	0	0
	$\nu_1$	55	44	45	58	36	45	60	36	42
MPW1PW91	$E$	–1302.743 17	–1302.776 52	–1302.771 67	–500.298 68	–500.324 29	–500.308 29	–501.247 14	–501.273 22	–501.261 29
	$\Delta E$	20.9	0.0	3.0	16.1	0.0	10.0	16.4	0.0	7.5
	Nimag	0	0	0	0	0	0	0	0	0
	$\nu_1$	55	49	43	58	42	42	56	40	37
B3LYP	$E$	–1302.855 56	–1302.878 05	–1302.872 44	–500.429 14	–500.445 15	–500.428 46	–501.377 65	–501.393 76	–501.381 06
	$\Delta E$	14.1	0.0	3.5	10.0	0.0	10.5	10.1	0.0	8.0
	Nimag	0	0	0	0	0	0	0	0	0
	$\nu_1$	54	50	43	57	42	43	57	40	37

**Table 9.** Dissociation Energies (in kcal/mol) for  $M(\text{CO})_n$  ( $n = 7, 6, 5$ )

	BP86			MPW1PW91			B3LYP		
	Ti	Zr	Hf	Ti	Zr	Hf	Ti	Zr	Hf
$M(\text{CO})_7(7S-1) \rightarrow M(\text{CO})_6(6S-1) + \text{CO}$	34.0	36.3	36.9	29.9	34.0	35.0	24.3	30.1	30.9
$M(\text{CO})_7(7S-1) \rightarrow M(\text{CO})_6(6T) + \text{CO}$	31.6	35.6	35.6	25.4	32.0	32.5	20.1	28.1	28.6
$M(\text{CO})_6(6S-1) \rightarrow M(\text{CO})_5(5S) + \text{CO}$	30.6	27.9	30.9	31.3	29.4	32.2	28.7	27.4	30.3
$M(\text{CO})_6(6T) \rightarrow M(\text{CO})_5(5S) + \text{CO}$	33.0	28.6	32.2	35.8	31.3	34.7	32.9	29.5	32.6
$M(\text{CO})_6(6T) \rightarrow M(\text{CO})_5(5T) + \text{CO}$	29.0	29.5	32.0	26.8	27.6	30.1	25.5	26.8	29.4
$M(\text{CO})_5(5S) \rightarrow M(\text{CO})_4(4T) + \text{CO}$	27.9	32.5	34.7	21.6	26.1	28.3	22.7	27.3	29.8
$M(\text{CO})_5(5T) \rightarrow M(\text{CO})_4(4T) + \text{CO}$	31.9	31.6	34.8	30.6	29.9	32.8	30.2	30.0	33.1

center with little ligand–ligand repulsion. The Zr and Hf analogues  $\text{Zr}(\text{CO})_7$  and  $\text{Hf}(\text{CO})_7$  have similar BDE values (Table 9). Thus there appears to be no fundamental problem in bonding seven CO groups to a single metal atom. This situation justifies our expectation that a stable seven-coordinated titanium, zirconium, or hafnium carbonyl can be prepared following the 18-electron rule.

The experimental observations show that a titanium carbonyl is a metastable compound which decomposes around 40–45 K.<sup>4</sup> Meyer and Armentrout<sup>9</sup> suggest that the BDEs for  $\text{Ti}(\text{CO})_n^+$  ( $n = 4, 5$ ) are due solely to electrostatic interactions. The covalent interactions play a dominant role in the bonding between the metal center and carbonyl ligands, and the covalent contributions appear to increase with an increasing number of coordinated CO ligands.<sup>7</sup> However, our theoretical results show that all of the dissociation energies for  $M(\text{CO})_n \rightarrow M(\text{CO})_{n-1} + \text{CO}$  for  $n = 7, 6$ , and 5 are  $\sim 30$  kcal/mol (Table 9).

### 3.3. Evidence for $\text{Ti}(\text{CO})_7$ in Low Temperature Matrices.

**3.3.1. Vibrational Spectra.** Tables 10–13 list the theoretical  $\nu(\text{CO})$  vibrational frequencies for  $\text{Ti}(\text{CO})_n$  ( $n = 7, 6, 5, 4$ ) obtained by the BP86 method, which is established to be the most reliable DFT method for predicting  $\nu(\text{CO})$  frequencies of the first-row transition metal–carbonyl derivatives.<sup>47</sup> The predicted  $\nu(\text{CO})$  frequencies for the lowest energy structures of  $\text{Ti}(\text{CO})_n$  ( $n = 6, 5, 4$ ) are seen to be very close to those reported by Zhou and Andrews.<sup>8</sup>

Thus the experimental 1946  $\text{cm}^{-1}$   $\nu(\text{CO})$  frequency assigned to  $\text{Ti}(\text{CO})_6$  corresponds to the pair of strong  $\nu(\text{CO})$  frequencies at 1958 and 1959  $\text{cm}^{-1}$  predicted by DFT for the lowest energy structure of  $\text{Ti}(\text{CO})_6$ , namely the  $D_{3d}$  distorted octahedral structure **6T** (Figure 1 and Table 11). The closely spaced predicted 1958 and 1959  $\text{cm}^{-1}$   $\nu(\text{CO})$

(47) Wang, H.; Xie, Y.; King, R. B.; Schaefer, H. F., III *J. Am. Chem. Soc.* **2005**, *127*, 11564.



**Table 10.** Harmonic Vibrational Frequencies  $\nu(\text{CO})$  ( $\text{cm}^{-1}$ ) for  $\text{M}(\text{CO})_7$  Predicted by the BP86 Method<sup>a</sup>

species	Ti(CO) <sub>7</sub>	expt <sup>d</sup>	Zr(CO) <sub>7</sub>	Hf(CO) <sub>7</sub>
<b>7-1</b> ( <i>C<sub>3v</sub></i> )	1946 (a <sub>1</sub> , 688)	1947 ± 3	1947 (a <sub>1</sub> , 524),	1946 (a <sub>1</sub> , 430),
	1952 (e, 1310)		1955 (e, 1326),	1952 (e, 1303),
	1970 (a <sub>1</sub> , 1020)	1985 ± 3	1965 (a <sub>1</sub> , 1322),	1962 (a <sub>1</sub> , 1474),
	1986 (e, 675)		1977 (e, 982),	1973 (e, 1036),
	2056 (a <sub>1</sub> , 68)		2059 (a <sub>1</sub> , 31)	2058 (a <sub>1</sub> , 30)
<b>7-2</b> ( <i>C<sub>s</sub></i> )	1892 (a', 325)		1851 (a', 371)	1825 (a', 382)
	1935 (a'', 688)		1941 (a'', 527)	1941 (a'', 482)
	1939 (a', 912)		1945 (a', 1039)	1944 (a', 1064)
	1962 (a', 2041)		1964 (a'', 1017)	1960 (a'', 1029)
	1964 (a'', 672)		1964 (a', 2337)	1962 (a', 2373)
	1972 (a'', 433)		1968 (a'', 408)	1965 (a'', 482)
	2041 (a', 31)		2046 (a', 52)	2045 (a', 58)

<sup>a</sup> The infrared intensities (km/mol, for only one component in case of degenerate modes) are in parentheses. The BKO experimental data<sup>d</sup> are also listed for comparison.

**Table 11.** Harmonic Vibrational Frequencies  $\nu(\text{CO})$  ( $\text{cm}^{-1}$ ) for  $\text{M}(\text{CO})_6$  Predicted by the BP86 Method<sup>a</sup>

species	Ti(CO) <sub>6</sub>	expt <sup>b</sup>	Zr(CO) <sub>6</sub>	Hf(CO) <sub>6</sub>
<b>6S-1</b> ( <i>D<sub>3d</sub></i> )	1941 (e <sub>g</sub> , 0)	1946	1937 (e <sub>g</sub> , 0)	1932 (e <sub>g</sub> , 0)
	1953 (e <sub>u</sub> , 2100)		1947 (a <sub>2u</sub> , 1091)	1943 (a <sub>2u</sub> , 1194)
	1958 (a <sub>2u</sub> , 1030)		1949 (e <sub>u</sub> , 2436)	1945 (e <sub>u</sub> , 2445)
	2048 (a <sub>1g</sub> , 0)		2046 (a <sub>1g</sub> , 0)	2046 (a <sub>1g</sub> , 0)
<b>6S-2</b> ( <i>C<sub>i</sub></i> )	1760 (a', 392)		1780 (a, 473)	1732 (a, 497)
	1928 (a', 917)		1927 (a, 664)	1928 (a, 740)
	1939 (a'', 1398)		1932 (a, 1397)	1933 (a, 1432)
	1941 (a', 142)		1938 (a, 304)	1936 (a, 250)
	1958 (a', 1467)		1954 (a, 2058)	1950 (a, 2092)
	2027 (a', 198)		2027 (a, 172)	2026 (a, 191)
<b>6T</b> ( <i>D<sub>3d</sub></i> )	1939 (e <sub>g</sub> , 0)	1946	1937 (e <sub>g</sub> , 0)	1934 (e <sub>g</sub> , 0)
	1958 (a <sub>2u</sub> , 2150)		1951 (e <sub>u</sub> , 1910)	1946 (e <sub>u</sub> , 1960)
	1959 (e <sub>u</sub> , 1660)		1953 (a <sub>2u</sub> , 2512)	1948 (a <sub>2u</sub> , 2540)
	2053 (a <sub>1g</sub> , 0)		2050 (a <sub>1g</sub> , 0)	2049 (a <sub>1g</sub> , 0)

<sup>a</sup> The infrared intensities (km/mol, of only one component for degenerate modes) are in parentheses.

**Table 12.** Harmonic Vibrational Frequencies  $\nu(\text{CO})$  ( $\text{cm}^{-1}$ ) for  $\text{M}(\text{CO})_5$  Predicted by the BP86 Method<sup>a</sup>

species	Ti(CO) <sub>5</sub>	expt <sup>b</sup>	Zr(CO) <sub>5</sub>	Hf(CO) <sub>5</sub>
<b>5S</b> ( <i>C<sub>3v</sub></i> )	1902 (a <sub>1</sub> , 457)	1885	1907 (a <sub>1</sub> , 255)	1905 (a <sub>1</sub> , 161)
	1922 (e, 1513)		1914 (e, 1642)	1912 (e, 1700)
	1940 (a <sub>1</sub> , 1812)	1912	1933 (a <sub>1</sub> , 2263)	1923 (a <sub>1</sub> , 2382)
	2027 (a <sub>1</sub> , 36)		2020 (a <sub>1</sub> , 7)	2018 (a <sub>1</sub> , 0)
<b>5T</b> ( <i>C<sub>4v</sub></i> )	1936 (e, 4142)		1929 (e, 2309)	1924 (e, 2358)
	1946 (b <sub>2</sub> , 0)		1935 (a <sub>1</sub> , 903)	1925 (a <sub>1</sub> , 967)
	1954 (a <sub>1</sub> , 742)		1937 (b <sub>2</sub> , 0)	1932 (b <sub>2</sub> , 0)
	2034 (a <sub>1</sub> , 17)		2027 (a <sub>1</sub> , 12)	2026 (a <sub>1</sub> , 5)
<b>5Q</b> ( <i>D<sub>3h</sub></i> )	1943 (e', 2606)		1923 (e', 1506)	1919 (e', 1514)
	1953 (a <sub>1</sub> ', 0)		1935 (a <sub>1</sub> ', 0)	1929 (a <sub>1</sub> ', 0)
	1970 (a <sub>2</sub> '', 1594)		1962 (a <sub>2</sub> '', 1860)	1953 (a <sub>2</sub> '', 1890)
	2032 (a <sub>1</sub> ', 0)		2023 (a <sub>1</sub> ', 0)	2021 (a <sub>1</sub> ', 0)

<sup>a</sup> The infrared intensities (km/mol, of only one component for degenerate modes) are in parentheses.

frequencies for  $\text{Ti}(\text{CO})_6$  are not likely to be resolved under the experimental conditions. Similarly the experimental  $\nu(\text{CO})$  frequencies<sup>8</sup> of 1885 and 1912  $\text{cm}^{-1}$  assigned to  $\text{Ti}(\text{CO})_5$  are within 40  $\text{cm}^{-1}$  of the most intense  $\nu(\text{CO})$  frequencies of 1922 and 1940  $\text{cm}^{-1}$  predicted for the *C<sub>3v</sub>* distorted trigonal bipyramid structure of  $\text{Ti}(\text{CO})_5$ , namely **5S** (Figure 2 and Table 12). Furthermore, the experimental  $\nu(\text{CO})$  frequencies of 1853 and 1871  $\text{cm}^{-1}$  assigned to  $\text{Ti}(\text{CO})_4$  by Zhou and Andrews<sup>8</sup> are consistent with the predicted strong  $\nu(\text{CO})$  frequencies of 1888 and {1913, 1914}  $\text{cm}^{-1}$  for the lowest energy structure of  $\text{Ti}(\text{CO})_4$ , namely the *C<sub>2v</sub>* triplet structure **4T**, derived from a trigonal bipyramid by removing

an equatorial vertex. This assumes, of course, that the predicted pair of frequencies at 1913 and 1914  $\text{cm}^{-1}$  are not resolved under the experimental conditions. This present research thus supports the assignments of some of the bands in the lowest temperature  $\nu(\text{CO})$  spectra of  $\text{Ti}/\text{CO}$  systems observed by Zhou and Andrews<sup>8</sup> to the  $\text{Ti}(\text{CO})_n$  species ( $n = 6, 5, 4$ ). Furthermore, this work also provides some insight into the structures of these unstable coordinatively unsaturated titanium species, so far observed only in low-temperature inert matrices.

None of the reported studies of  $\text{Ti}/\text{CO}$  matrices<sup>4,6–8</sup> suggested  $\text{Ti}(\text{CO})_7$  as one of the products. However, our theoretical studies

**Table 13.** Harmonic Vibrational Frequencies  $\nu(\text{CO})$  ( $\text{cm}^{-1}$ ) for  $\text{M}(\text{CO})_4$  Predicted by the BP86 Method<sup>a</sup>

species	Ti(CO) <sub>4</sub>	expt <sup>b</sup>	Zr(CO) <sub>4</sub>	Hf(CO) <sub>4</sub>
<b>4S</b> ( <i>T<sub>d</sub></i> )	1894 (t <sub>2</sub> , 5580)		1884 (t <sub>2</sub> , 1927)	1878 (t <sub>2</sub> , 1946)
	2001 (a <sub>1</sub> , 0)		1986 (a <sub>1</sub> , 0)	1984 (a <sub>1</sub> , 0)
<b>4T</b> ( <i>C<sub>2v</sub></i> )	1888 (b <sub>1</sub> , 923)	1853	1880 (b <sub>1</sub> , 918)	1878 (b <sub>1</sub> , 932)
	1914 (b <sub>2</sub> , 2322)	1871	1904 (a <sub>1</sub> , 797)	1897 (a <sub>1</sub> , 834)
	1913 (a <sub>1</sub> , 700)		1907 (b <sub>2</sub> , 2489)	1899 (b <sub>2</sub> , 2522)
	2001 (a <sub>1</sub> , 24)		1991 (a <sub>1</sub> , 41)	1986 (a <sub>1</sub> , 41)
<b>4Q</b> ( <i>C<sub>3v</sub></i> )	1924 (e, 3032)		1903 (e, 1643)	1896 (e, 1668)
	1935 (a <sub>1</sub> , 715)		1913 (a <sub>1</sub> , 778)	1903 (a <sub>1</sub> , 867)
	2003 (a <sub>1</sub> , 54)		1983 (a <sub>1</sub> , 90)	1980 (a <sub>1</sub> , 54)

<sup>a</sup> The infrared intensities (km/mol, of only one component for degenerate modes) are in parentheses.

**Table 14.** Comparison of Calculated Electronic Transitions for Ti(CO)<sub>6</sub> and Ti(CO)<sub>7</sub> with the BKO Experimental Data<sup>4</sup>

Ti(CO) <sub>7</sub> ( <b>7S-1</b> )		Ti(CO) <sub>6</sub> ( <b>6S-1</b> )		Ti(CO) <sub>6</sub> ( <b>6T</b> )		expt <sup>14</sup>
energy (nm)	oscillator strength	energy (nm)	oscillator strength	energy (nm)	oscillator strength	transition energies in $\text{cm}^{-1}$ and nm
482	$0.0041 \times 2$			440	$0.0131 \times 2$	
				378	$0.0063 \times 2$	
345	$0.0147 \times 2$	346	0.0247	352	0.0173	(27 174) 368 w
287	$0.0432 \times 2$					(29 762) 336 w
268	$0.1260 \times 2$					(33 898) 295 s
252	$0.0387 \times 2$					(38 023) 263 m

of the  $\nu(\text{CO})$  frequencies of  $\text{Ti}(\text{CO})_n$  derivatives (Tables 10–13) suggest that the species claimed by Busby, Klotzbücher, and Ozin (BKO)<sup>4</sup> to be  $\text{Ti}(\text{CO})_6$  could instead be  $\text{Ti}(\text{CO})_7$  provided that the following reasonable assumptions are made: (1) the theoretical a<sub>1</sub>  $\nu(\text{CO})$  band at  $2056 \text{ cm}^{-1}$  with  $\sim 5\%$  of the theoretical intensity of the strongest  $\nu(\text{CO})$  frequency (Table 10) is too weak to be observed in the matrix isolation experiments; (2) the theoretical strong pairs of  $\nu(\text{CO})$  frequencies at  $1946$  and  $1952 \text{ cm}^{-1}$  and at  $1970$  and  $1986 \text{ cm}^{-1}$  are too close together to be resolved in most of the matrix isolation experiments. The latter assumption is supported by the breadth of the  $\nu(\text{CO})$  bands in the figures of the BKO paper.<sup>4</sup> If the average of the four major bands in our calculations are grouped as doublets, then our BP86 calculations predict two strong infrared  $\nu(\text{CO})$  bands at  $1952$  and  $1986 \text{ cm}^{-1}$  for  $\text{Ti}(\text{CO})_7$ . These theoretical  $\nu(\text{CO})$  bands are remarkably close to the experimental  $\nu(\text{CO})$  bands at  $1947 \pm 3$  and  $1985 \pm 3 \text{ cm}^{-1}$  found for the reaction product of titanium atoms with carbon monoxide. We therefore suggest that this reaction product might be  $\text{C}_{3v}$  capped octahedral  $\text{Ti}(\text{CO})_7$  rather than  $\text{Ti}(\text{CO})_6$ . The following further supports formulation of this reaction product as  $\text{Ti}(\text{CO})_7$ : (1) In the CO matrix experiments of BKO the lower  $\nu(\text{CO})$  band is resolved into two components at  $1945$  and  $1953 \text{ cm}^{-1}$  which are only  $1 \text{ cm}^{-1}$  from our predicted frequencies of  $1946$  and  $1952 \text{ cm}^{-1}$ ; (2) The  $\nu(\text{CO})$  frequencies for the global minima of  $\text{Ti}(\text{CO})_5$  and  $\text{Ti}(\text{CO})_4$  (Tables 12 and 13) are very different in positions and intensities from those observed in the matrix isolation experiments.

**3.3.2. Electronic Spectra.** In order to obtain additional evidence for the presence of  $\text{Ti}(\text{CO})_7$  in low-temperature matrices, we have computed the excited states between 250 and 500 nm of **7S-1**, **6S-1**, and **6T** for  $\text{Ti}(\text{CO})_n$  systems using the CI-Single method based on the BP86/DZP geometries (Table 14). The experimentally observed four electronic transitions in the 375 to 250 nm range are seen to correspond fairly closely to the four calculated electronic transitions for  $\text{Ti}(\text{CO})_7$  (**7S-1**). More specifically, our calculations predict a strong electronic transition for **7S-1** in this range at 268 nm. This is very close to the strongest observed<sup>4</sup> electronic transition at 263 nm in

the low temperature matrices. By contrast, no electronic transitions below 340 nm are predicted for either singlet  $\text{Ti}(\text{CO})_6$  (**6S-1**) or triplet  $\text{Ti}(\text{CO})_6$  (**6T**). Thus the electronic spectrum of the BKO product<sup>4</sup> in the low-temperature matrices provides additional evidence for the presence of  $\text{Ti}(\text{CO})_7$  rather than  $\text{Ti}(\text{CO})_6$  in these matrices.

This evidence for  $\text{Ti}(\text{CO})_7$  as one of the products in certain low temperature matrix experiments<sup>4</sup> suggests further investigations of such systems under conditions where carbonyl-rich product formation is most likely. In view of the complexity of the Ti/CO system, related studies on analogous Zr/CO and Hf/CO systems are indicated seeking conditions where carbonyl-rich species can be performed. The existing experimental work<sup>13</sup> on Zr/CO and Hf/CO systems report species with a maximum of five carbonyl groups per metal atom.

#### 4. Conclusions

The equilibrium geometries, thermochemistry, and vibrational frequencies of the homoleptic metal–carbonyls of the group 4 elements,  $\text{M}(\text{CO})_n$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}; n = 7, 6, 5, 4$ ), are relatively consistent for the different central metal atoms. Thus the global minima for the 18-electron  $\text{M}(\text{CO})_7$  molecules are all singlet  $\text{C}_{3v}$  capped octahedra. The global minima for the 16-electron  $\text{M}(\text{CO})_6$  species are triplet  $\text{M}(\text{CO})_6$  structures distorted from  $O_h$  symmetry to  $D_{3d}$  symmetry. However, the corresponding singlet  $\text{M}(\text{CO})_6$  structures lie within 5 kcal/mol of the triplet global minima. The global minima for  $\text{M}(\text{CO})_n$  ( $n = 5, 4$ ) are triplet structures derived from the  $D_{3d}$  distorted octahedral structures of  $\text{M}(\text{CO})_6$  by removal of one or two CO groups, respectively. Quintet  $D_{3h}$  trigonal bipyramidal structures for  $\text{M}(\text{CO})_5$  and singlet  $T_d$  tetrahedral structures for  $\text{M}(\text{CO})_4$  are also found, as well as higher energy structures for  $\text{M}(\text{CO})_6$  and  $\text{M}(\text{CO})_7$  containing a unique CO group bonded to the metal atom through both M–C and M–O bonds. The dissociation energies  $\text{M}(\text{CO})_7 \rightarrow \text{M}(\text{CO})_6 + \text{CO}$  are substantial, indicating no fundamental problem in bonding seven CO groups to a single metal atom.

The  $\nu(\text{CO})$  frequencies for  $\text{M}(\text{CO})_n$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}; n = 6, 5, 4$ ) predicted by the BP86 method correspond rather closely to those found by Zhou and Andrews<sup>8,13</sup> in the product mixtures

from reactions of laser ablated metal atoms with carbon monoxide in inert low temperature matrices. No evidence for  $M(\text{CO})_7$  for any of the three metals has yet been suggested from these experiments despite the fact that our theoretical studies predict  $M(\text{CO})_7$  to be reasonable molecules for all three group 4 metals. Earlier experimental studies by Busby, Klotzbücher, and Ozin<sup>4</sup> on reactions of titanium atoms with carbon monoxide in inert matrices gave a product claimed by them to be  $\text{Ti}(\text{CO})_6$ . However, the  $\nu(\text{CO})$  frequencies and electronic spectra found by them for this product agree well with those predicted by our theoretical studies for the elusive  $\text{Ti}(\text{CO})_7$  (Table 10). We therefore think that BKO may have obtained  $\text{Ti}(\text{CO})_7$  more than 30 years ago without realizing it, since reliable theoretical methods to predict structures, infrared vibrational frequencies, and electronic spectra were not available at the time of their work.

**Acknowledgment.** We are indebted to the 111 Project (B07012) in China, China Postdoctoral Science Foundation (20070410139), Fund for the Doctoral Program of Higher Education (20070533142), and the U.S. National Science Foundation (Grants CHE-0209857, CHE-0749868, and CHE-0716718) for support of this research.

**Supporting Information Available:** Complete Gaussian reference (ref 40); Table 1: comparison of calculations on the titanium carbonyls  $\text{Ti}(\text{CO})_n$  using the all-electron DZP (14s11p6d/10s8p3d) basis set and Stuttgart/Dresden double- $\zeta$  (SDD) ECP basis sets. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA8003655