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Structures and Bond Energies of the Transition Metal Hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W). A Theoretical Study[1]

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Abstract: The geometries of the hexacarbonyls and pentacarbonyls of chromium, molybdenum, and tungsten are optimized at the Hartree–Fock and MP2 levels of theory using effective core potentials for the metal atoms. The M–CO bond lengths of $Mo(CO)_6$ and $W(CO)_6$ predicted at the MP2 level using moderate valence basis sets are in excellent agreement with experimental values. The Cr–CO bond length in $Cr(CO)_6$ calculated at MP2 is too short. The total bond energies of the metal hexacarbonyls calculated at the CCSD(T) level of theory are slightly lower than the experimentally derived values. The first dissociation energies calculated at CCSD(T) using MP2-optimized geometries for $M(CO)_6$ and $M(CO)_5$ are in very good agreement with experimental results for $Mo(CO)_6$ and $W(CO)_6$ from gas-phase laser pyrolysis. The calculated first dissociation energy at CCSD(T) for $Cr(CO)_6$ using the MP2-optimized geometries for $Cr(CO)_6$ and $Cr(CO)_5$ is too high. The theoretical and experimental results suggest the following first dissociation energies ΔH^{298} for the $M(CO)_6$ compounds: $Cr(CO)_6 = 37 \pm 2$ kcal/mol; $Mo(CO)_6 = 40 \pm 2$ kcal/mol; $W = 46 \pm 2$ kcal/mol. The agreement of previously reported theoretical dissociation energies using density functional theory with kinetic data for the activation energy of substitution reactions showing a different order for the hexacarbonyls Mo < Cr < W is misleading. The kinetic data for $Mo(CO)_6$ and $W(CO)_6$ refer to a different mechanism and should not be used to estimate the metal–carbonyl bond strength.

1. Introduction

There is a widespread belief that transition metal complexes cannot be calculated accurately by ab initio methods, unlike compounds of first-, second-, and third-row elements for which systematic studies have proven the usefulness and reliability of quantum mechanical ab initio calculations.[2] At present, there are two theoretical methods available which may change the pessimistic outlook in the near future, that is density functional theory (DFT)[3] and effective core potentials (ECP).[4] We have started to investigate systematically the performance of ECP methods and found that the geometries of saturated transition metal complexes in *high* oxidation states can theoretically be predicted in good agreement with experiment[1,5–7] at the Hartree–Fock level using standard contraction schemes suggested by us.[5] Similar results have also been found by other groups.[8]

The situation is different, however, for transition metal complexes in *low* oxidation states. It is well-known that the metal–CO bond distances in carbonyl complexes with the oxidation state 0 are calculated to be too long at the HF level of theory.[9–15] Also, the relative bond lengths of the axial and equatorial Fe–CO bonds are predicted to be opposite of what is experimentally found.[10,11] In a recent study by Barnes et al. of $Cr(CO)_6$ at a very high level of theory it was concluded that the geometry of $Cr(CO)_6$ can be calculated in good agreement with experiment at CCSD(T) using a rather large basis set.[16a] Theoretical studies at this level would be prohibitive for most transition metal compounds, in particular for transition metals of the second and third row, but we have recently shown[1] that the geometries of $Ag(CO)_2^+$ and $Au(CO)_2^+$ are calculated at the MP2 level of theory using standard ECP valence basis sets[17] in reasonable agreement with experiment.[18] This encouraged us to study other transition metal carbonyl complexes at the MP2 level using different ECPs. Here we report the theoretically predicted geometries for $M(CO)_6$ and $M(CO)_5$ (M = Cr, Mo, W) using three different types of ECPs described below.

An even more challenging aspect of transition metal complexes for both theory and experiment is the accurate determination of

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bond energies.[19] It is disturbing that, even for basic compounds such as the hexacarbonyls of chromium, molybdenum, and tungsten, the first dissociation energy of a carbonyl ligand is still controversial.[20–22]

$$M(CO)_6 \rightarrow M(CO)_5 + CO \qquad (1)$$

The knowledge of the exact dissociation energies for reaction 1 is very important for the large class of transition metal carbonyl complexes,[23] because in substitution reactions following the dissociative/associative mechanism the first dissociation energy is equal to the activation energy of the reaction. There are conflicting theoretical[24] and experimental[20–22] data for the energy of reaction 1 for M = Cr, Mo, and W reported in the literature. The results of kinetic measurements[20] and photoacoustic calorimetry[21] indicate that the first CO bond energy of Mo(CO)$_6$ is *lower* than that for Cr(CO)$_6$ and W(CO)$_6$. However, recent mechanistic studies of the substitution reactions of complexes M(CO)$_5$(THF) M = Cr, Mo, W) give evidence for a gradual changeover in mechanism from a more dissociative to a more associative activation process along the series Cr, Mo, W.[25] This leaves some doubts whether the kinetic data[20] can be used to estimate the metal–carbonyl bond energies for the heavier metal hexacarbonyls.

The only set of experimental data for reaction 1 in the gas phase is reported by Lewis et al.[22] Using pulsed laser pyrolysis techniques, these authors report dissociation energies for the hexacarbonyls which show an increase for the first binding energy in the order Cr < Mo < W.[22] The only theoretical study devoted to the set of first bond energies of M(CO)$_6$ molecules was reported by Ziegler and co-workers[24] using DFT techniques.[3] Surprisingly, the results obtained using the local density approximation (LDA) with nonlocal corrections (NL) support the values obtained by measurements in solution[20,21] showing the order Mo < Cr < W.[24] However, in the theoretical studies no corrections were made for zero-point vibrational energies or for thermal contributions. Also, the calculations for the pentacarbonyls were carried out using the same geometries as the hexacarbonyls. Because the knowledge about the first dissociation energies of M(CO)$_6$ (M = Cr, Mo, W) molecules is important for the chemistry of the large class of carbonyl complexes of these elements,[23] we decided to carry out ab initio calculations based upon optimized geometries. We report calculated total bond energies and the first dissociation energies at optimized geometries using coupled cluster (CC) theory[26a] with singles and doubles and a noniterative estimate of the contributions due to the triples (CCSD(T))[26] in conjunction with ECP wave functions. Thus, the results presented here allow an estimate of the approximations made in the DFT study by Ziegler et al.[24] and give a comparison of the accuracy of the two methods.

Table 1. Basis Sets Used in This Study

basis set	metal basis set	CO basis set	no. of basis functions for M(CO)$_6$
I	HW3DZ (441/41/41)	3-21G	127
II	HW3DZ2P (441/2111/41)	6-31G(d)	193
III	SP (31111/4111/411)	6-31G(d)	200/195[a]
IV	SKBJ (4121/4121/311)	6-31G(d)	199

[a] For Mo and W one less d-function is used.

2. Theoretical Methods

The geometry optimizations have been carried out using three different sets of ECPs for the metal atoms. The first ECP is the small-core set developed by Hay and Wadt[17] (HW), the second by Stoll, Preuss, and co-workers[27] (SP), and the third by Stevens, Krauss, Basch, and Jasien[28] (SKBJ). The three ECPs have the same core size, treating explicitly the $(n-1)s^2$, $(n-1)p^6$, $(n-1)d^x$, and $(n)s^y$ electrons of the transition metal. Thus, Cr, Mo, and W are calculated with 14 "valence" electrons. There are differences, however, in the way in which the pseudopotentials are derived. HW[17] optimized the ECPs from numerical Hartree–Fock calculations adjusted to orbital energies of a single atomic reference state. The ECPs of HW include relativistic terms only for elements of the second and third row of the transition metals, but not for the first row. Thus, relativistic effects are included for Mo and W, but not for Cr. The ECPs of SP[27] have the same analytical form for the potentials as the ECPs of HW, but they are fitted to quantum mechanical observables such as ionization and excitation energies for several excited states, including relativistic corrections for all three rows of the transition metals. SKBJ[28] published "compact" potentials developed by applying an energy-overlap functional which also includes relativistic effects for all three rows of the transition metals.

Table 1 shows the valence basis sets used in this study. Basis set I employs the small-core ECP developed by HW,[17] using a (441/41/$N$1) contraction scheme (N = 4, 3, 2 for Cr, Mo, W, respectively) suggested by us[5] in conjunction with a 3-21G basis set[29] for C and O. Basis set II is used with the less contracted ECP by HW (441/2111/$N$1) for the transition metals combined with a 6-31G(d)[30] basis set for C and O. Basis set III has the ECP valence basis set of SP[27] contracted to (31111/4111/411) and 6-31G(d) for C and O. The ECP by SKBJ[28] with the contraction (4121/4121/311) in conjunction with 6-31G(d) for C and O is used in basis set IV.

The geometries of M(CO)$_6$, M(CO)$_5$, and CO have been optimized with O_h symmetry for ($^1A_{1g}$) M(CO)$_6$ and C_{4v} symmetry for ($^1A_1$) M(CO)$_5$ at the restricted Hartree–Fock (RHF) and MP2[31] level of theory using basis sets I–IV. The vibrational frequencies and zero-point vibrational energies (ZPE) have been computed at HF/I only. Improved total energies are calculated at the CCSD(T) level using basis set II at geometries optimized at MP2/II. The 1s electrons of carbon and oxygen are kept frozen in the CCSD(T) calculations, but the $(n-1)$s and $(n-1)$p electrons are included. The metal atoms were calculated in the ^{7}S state. For the calculations of the geometries and vibrational frequencies the programs TURBOMOLE[32] and Gaussian 92[33] are used. The CCSD(T) calculations have been performed using the program ACES II.[34]

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Table 2. Previously Calculated Metal–Carbon Bond Lengths of $M(CO)_6$

metal	basis set M	basis set C, O	method	r(M–C)/ Å	ref
Cr	STO-3G	STO-3G	HF	1.789	57a
	(333/33/3)		HF	1.897	57b
	(5333/53/5)	(53/5)	HF	1.96	9
	(432/421/31)	(321/21)	HF	1.915	10
	[8s6p4d]	[4s3p]	HF	1.998	16a
	[8s6p4d]	[4s3p]	MCPF	1.954	16a
	[8s6p4d]	[4s3p]	CCSD	1.950	16a
	[8s6p4d]	[4s3p]	CCSD(T)	1.939	16a
	[8s6p4d1f]	[4s3p1d]	MCPF	1.940	16a
	[8s6p4d]	[4s3p]	MCPF	1.956	16b
	ext DZ	ext DZ	LCAO-Xα	1.869	57c
	DZ	DZ+P	LDA	1.874	36a
	TZ+3P	TZ+2P	LDA/NL-P	1.928	36b
	TZ+3P	TZ+2P	LDA/NL-SCF	1.916	36b
	TZ+3P	DZ+P	LDA	1.872	36c
	TZ+3P	DZ+P	LDA/NL	1.909	36c
	exp			1.914	35a
Mo	(43221/4221/ 321)	(321/21)	HF	2.101	12
	(21/21/31)	(321/21)	ECP[13]	2.092	12
	(541/41/31)	(321/21)	ECP[10]	2.122	12
	exp			2.063	35b

3. Geometries

Table 2 shows the calculated geometries for $Cr(CO)_6$ and $Mo(CO)_6$ reported in earlier studies in comparison with experiment.[35] There is no theoretical study reporting a geometry optimization of $W(CO)_6$ known to us. At the HF level using a minimal basis set, the Cr–CO distance is calculated to be too short. The theoretically predicted Cr–CO bond length becomes longer than the experimental value when larger basis sets are employed. This is also found for $Mo(CO)_6$; the calculated Mo–CO bond length at the HF level is 0.04–0.06 Å longer than experimentally reported. The Cr–CO bond is calculated shorter at the correlated level using MCPF wave functions[16] or at CCSD and CCSD(T).[16a] A better agreement with the experimentally reported Cr–CO bond length was calculated at CCSD(T) using the [8s6p4d] contracted basis set for Cr.[16a] However, the theoretical value (1.939 Å) is still 0.025 Å longer than the experimental value (1.914 Å). It was concluded that a better agreement with experiment would be obtained at the CCSD(T) level if the larger [8s6p4d1f] basis set for Cr is employed.[16a] However, calculations at this level of theory would be extremely expensive. More promising are the results which are reported using the LDA with nonlocal corrections (LDA/NL). The calculated Cr–CO bond lengths of $Cr(CO)_6$ using different nonlocal corrections by Fan and Ziegler[36b,c] (1.916, 1.909 Å) are very close to the experimental value.

Table 3 shows the optimized bond lengths for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ at the HF and MP2 level using basis sets I–IV. The calculated M–CO bond is always predicted to be too long at the HF level employing the four different basis sets. The higher-quality basis set II yields slightly longer M–CO bonds than basis set I. There are only marginal differences for the optimized M–CO interatomic distance among basis sets II, III, and IV, which means that relativistic effects appear to be negligible for the calculation of the bond lengths of chromium carbonyl complexes. The theoretically predicted M–CO bond lengths become shorter at the MP2 level. The Cr–CO bond is calculated to be too short by 0.05–0.03 Å. *But the theoretically predicted Mo–CO and W–CO bond lengths calculated at MP2 using either basis set II, III, or IV are in excellent agreement with the experimental values.* Interestingly, a good agreement between theoretical and experimental values for the Mo–CO and W–CO bond lengths is already found at MP2/I. It seems that the bond lengths of closed-shell transition metal carbonyl complexes for second- and third-row transition metals can be calculated with good accuracy at the MP2 level using ECPs and rather moderate valence basis sets.[37]

The calculated geometries for the metal pentacarbonyls are shown in Table 4. The calculations were carried out for the $^1A_1$ state of $M(CO)_5$ with C_{4v} symmetry. Previous theoretical[38] and experimental[39] studies indicate a square pyramidal (C_{4v}) ground state for the $M(CO)_5$ molecules. At the SCF level of theory, the geometries of $Cr(CO)_5$ are only slightly perturbed from the $Cr(CO)_6$ structures (Table 4). The axial Cr–CO distance becomes a bit shorter, but the equatorial Cr–CO distance is nearly the same as in the hexacarbonyl. The shortening of the axial M–CO bonds calculated at the HF level is significantly larger for $Mo(CO)_5$ and $W(CO)_5$. The M–CO_{ax} bonds are predicted to be 0.10–0.13 Å shorter than M–CO_{eq} for $Mo(CO)_5$ and $W(CO)_5$.

The M–CO bonds of $M(CO)_5$ calculated at the MP2 level are clearly shorter than at the SCF level (Table 4). In particular, the axial and equatorial Cr–CO bonds in $Cr(CO)_5$ are predicted to be much shorter at MP2 than at the SCF level. Previous theoretical studies of $Cr(CO)_5$ at correlated levels show also a shortening of the Cr–CO bond relative to the SCF values, albeit to a lesser extent.[16a] Because the optimized geometries for $M(CO)_6$ predicted at the MP2 level are in good agreement with experiment for M = Mo and W, but not for Cr, it seems possible that the same holds true for the pentacarbonyls. This assumption is supported by calculations of $M(CO)_5$ carried out at the CCSD(T)/II level using geometries optimized at MP2/II and using frozen geometries taken from the hexacarbonyls. For $Cr(CO)_5$, the CCSD(T)/II energy calculated with the frozen geometry is 3.0 kcal/mol lower than that using the MP2/II-optimized geometry. For $Mo(CO)_5$ and $W(CO)_5$ the MP2/II-optimized geometries are lower in energy at CCSD(T)/II than the frozen geometries by 0.6 (Mo) and 1.1 kcal/mol (W). This indicates that the MP2/II-optimized geometries for $Mo(CO)_5$ and $W(CO)_5$ should be quite reliable, but not those for $Cr(CO)_5$.

The M–C–O bond angle β is calculated at the MP2 level as being slightly smaller than that at the HF level. A surprising result of the geometry optimizations at the MP2 level for the pentacarbonyls is the predicted bond angle α between the axial and equatorial carbonyl groups (Table 4). The bond angle $\alpha(C_{ax}MC_{eq})$ is calculated as slightly *smaller* than 90° for the metal pentacarbonyls. From the intensity ratio of the A_1 vibrations of $M(CO)_5$ molecules observed in low-temperature matrix studies it was concluded that the pentacarbonyls of Cr, Mo, and W have bond angles between 90° and 95°.[39] Previous theoretical studies of $Cr(CO)_5$ and $Mo(CO)_5$ give values of ~92°.[16,38] It should be noted, however, that all previous geometry optimizations of the pentacarbonyls[16,38] with a *complete* geometry optimization have been carried out at the SCF level only. Theoretical studies at correlated levels[16] used geometries which either were assumed or the bond angles were frozen at the HF-optimized values. Table

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Table 3. Theoretical and Experimental Bond Lengths (Å) of $M(CO)_6$ (M = Cr, Mo, W) and CO

		r(M–C)			r(C–O)			
basis	method	M = Cr	M = Mo	M = W	M = Cr	M = Mo	M = W	C–O
I	HF	1.9764	2.1158	2.0919	1.1365	1.1363	1.1378	1.1289
II	HF	2.0093	2.1356	2.1064	1.1197	1.1199	1.1215	1.1137
III	HF	2.0068	2.1246	2.1235	1.1197	1.1204	1.1213	
IV	HF	2.0158	2.1372	2.1013	1.1196	1.1196	1.1219	
I	MP2	1.8597	2.0621	2.0623	1.1881	1.1839	1.1849	1.1712
II	MP2	1.8613	2.0608	2.0597	1.1676	1.1643	1.1655	1.1511
III	MP2	1.8692	2.0528	2.0716	1.1681	1.1647	1.1653	
IV	MP2	1.8827	2.0659	2.0534	1.1678	1.1644	1.1659	
exp[a]		1.918	2.063	2.058	1.141	1.145	1.148	1.1150[b]

[a] Reference 35a. [b] Reference 58.

Table 4. Calculated Bond Lengths (Å) and Angles (deg) of the Pentacarbonyls $M(CO)_5$ (M = Cr, Mo, W)

		HF				MP2			
		I	II	III	IV	I	II	III	IV
$Cr(CO)_5$	$r(M\text{–}C_{ax})$/Å	1.9685	1.9823	1.9773	1.9874	1.7585	1.7438	1.7529	1.7735
	$r(M\text{–}C_{eq})$/Å	1.9822	2.0085	2.0044	2.0141	1.8802	1.8736	1.8791	1.8913
	$r(C\text{–}O_{ax})$/Å	1.1361	1.1213	1.1214	1.1211	1.2128	1.1917	1.1938	1.1934
	$r(C\text{–}O_{eq})$/Å	1.1377	1.1208	1.1208	1.1207	1.1858	1.1666	1.1669	1.1663
	$\alpha(C_{ax}\text{–}M\text{–}C_{eq})$	91.9	92.4	92.5	92.4	87.7	86.1	86.0	86.0
	$\beta(M\text{–}C_{eq}\text{–}O_{eq})$[a]	179.3	179.4	179.3	179.2	175.2	173.7	173.6	173.4
$Mo(CO)_5$	$r(M\text{–}C_{ax})$/Å	2.0302	2.0333	2.0226	2.0352	1.9466	1.9296	1.9233	1.9352
	$r(M\text{–}C_{eq})$/Å	2.1202	2.1371	2.1248	2.1367	2.0664	2.0604	2.0522	2.0631
	$r(C\text{–}O_{ax})$/Å	1.1417	1.1272	1.1278	1.1266	1.1968	1.1787	1.1794	1.1783
	$r(C\text{–}O_{eq})$/Å	1.1366	1.1202	1.1208	1.1200	1.1845	1.1650	1.1657	1.1652
	$\alpha(C_{ax}\text{–}M\text{–}C_{eq})$	90.2	90.6	90.6	90.5	88.2	87.6	87.8	86.9
	$\beta(M\text{–}C_{eq}\text{–}O_{eq})$[a]	178.4	178.6	178.6	178.4	176.2	175.7	176.0	175.0
$W(CO)_5$	$r(M\text{–}C_{ax})$/Å	2.0000	1.9998	2.0122	1.9924	1.9583	1.9440	1.9473	1.9353
	$r(M\text{–}C_{eq})$/Å	2.0897	2.1031	2.1213	2.0900	2.0589	2.0534	2.0664	2.0490
	$r(C\text{–}O_{ax})$/Å	1.1454	1.1311	1.1305	1.1317	1.959	1.1778	1.1787	1.1785
	$r(C\text{–}O_{eq})$/Å	1.1385	1.1220	1.1218	1.1224	1.1865	1.1671	1.1668	1.1676
	$\alpha(C_{ax}\text{–}M\text{–}C_{eq})$	90.3	90.6	90.6	90.3	88.9	88.9	88.4	86.84
	$\beta(M\text{–}C_{eq}\text{–}O_{eq})$[a]	178.5	178.4	178.5	178.0	176.9	177.0	176.5	175.3

[a] The equatorial oxygen is trans with regard to the axial CO group.

Table 5. Calculated Total Energies E_{tot} (au) of $M(CO)_6$, $M(CO)_5$ (M = Cr, Mo, W) and CO[a]

basis	method	$Cr(CO)_6$	$Mo(CO)_6$	$W(CO)_6$	$Cr(CO)_5$	$Mo(CO)_5$	$W(CO)_5$	CO
I	HF	–758.166 45	–739.576 03	–739.861 33	–646.026 43	–627.426 91	–627.698 53	–112.093 30
		(32.6)	(32.2)	(32.8)	(26.7)	(26.7)	(27.2)	(3.3)
II	HF	–761.978 24	–743.385 59	–743.669 03	–649.207 52	–630.606 37	–630.876 30	–112.308 21
III	HF	–762.650 86	–744.043 38	–742.904 90	–649.880 78	–631.261 79	–630.116 02	
IV	HF	–762.228 12	–743.842 02	–743.626 67	–649.457 00	–631.061 86	–630.834 89	
I	MP2	–759.962 20	–741.170 00	–741.433 43	–647.546 45	–628.776 82	–629.029 26	–112.737 34
II	MP2	–764.290 85	–745.466 49	–745.732 14	–651.177 78	–632.372 43	–632.623 55	–113.020 64
III	MP2	–765.024 64	–746.131 45	–744.970 91	–651.908 89	–633.035 81	–631.869 07	
IV	MP2	–764.623 96	–745.973 75	–745.697 83	–651.505 26	–632.876 63	–632.589 78	
II	CCSD(T)	–764.244 25	–745.495 44	–745.759 70	–651.137 51	–632.397 39	–632.649 40	–113.033 76

[a] ZPE values (kcal mol^{-1}) are given in parentheses.

4 shows that bond angles between 90.2° and 92.5° are predicted at the HF level using basis sets I–IV. Bond angles <90° are predicted only at MP2. In order to find out if this is an artifact of MP2, we calculated the energies of the pentacarbonyls at CCSD(T)/II using the optimized geometries at MP2/II but with $\alpha = 92°$. For $Cr(CO)_5$, the energy calculated at CCSD(T) with $\alpha = 92°$ is 0.3 kcal/mol *lower* than that with $\alpha = 86.1°$. The total energy of $Mo(CO)_5$ and $W(CO)_5$ calculated at CCSD(T) with $\alpha = 92°$ is 1.1 (Mo) and 0.5 (W) kcal/mol *higher* than that with $\alpha = 87.6°$ and 88.9°, respectively. Thus, the CCSD(T) energies support the theoretically predicted bond angles $\alpha < 90°$ for $Mo(CO)_5$ and $W(CO)_5$.

The calculated bond angles $\alpha < 90°$ for $M(CO)_5$ molecules appear to be at variance with the experimental results obtained from the analysis of the IR intensities observed for the pentacarbonyls in matrices.[39] However, the bond angles deduced from measurements of the intensity ratio show considerable differences when measured in different matrices. For $Cr(CO)_5$, a bond angle α of 94.1° was measured in Ar, but a value of 92.8° was observed in CH_4.[39b] It is conceivable that the experimentally observed data refer to weakly bound hexacoordinated complexes $M(CO)_5X$ rather than free $M(CO)_5$. Rare gas–metal carbonyl complexes $M(CO)_5X$ with X = Ar, Kr, and Xe are known, and the M–Xe bond energy has been measured as 8–9 kcal/mol.[40] The weak interaction between $M(CO)_5$ and molecules X from the "inert" matrix might then be responsible for the umbrella shift from $\alpha < 90°$ to $\alpha > 90°$. It should also be noted that the position of the visible band in the UV–visible spectra of $M(CO)_5$ was found to be extraordinarily sensitive to the matrix material used.[39c]

4. Dissociation Energies

Table 5 shows the energies of the calculated compounds. Table 6 shows the theoretical and experimental results for the first dissociation energy of the $M(CO)_6$ molecules. The bond energies calculated in this study are based upon geometries optimized at MP2/II.

We compare first the two sets of theoretical data predicted by the ECP method at the CCSD(T) level of theory and the DFT/

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[40] Wells, J. R.; Weitz, E. *J. Am. Chem. Soc.* **1992**, *114*, 2783.

[41] Sherwood, D. E.; Hall, M. B. *Inorg. Chem.* **1983**, *22*, 93.

Table 6. Theoretically Predicted and Experimentally Observed First Dissociation Energies (kcal mol^{-1})

M	ΔE^{a}	$\Delta H^{\circ\,a}$	$\Delta H^{298\,a}$	$\Delta E_{calc}{}^{c}$	$\Delta H_{exp}{}^{d}$	$\Delta H_{exp}{}^{e}$	$\Delta H_{exp}{}^{f}$
Cr	45.8 (32.5[b])	43.2 (29.9[b])	45.3 (32.0[b])	35.1	38.7	37 ± 5	36.8 ± 2
Mo	40.4	38.2	40.3	28.4	30.1	34 ± 5	40.5 ± 2
W	48.0	45.7	47.8	33.9	39.7	38 ± 5	46.0 ± 2

[a] Calculated at CCSD(T)/II using MP2/II-optimized geometries. [b] Calculated at CCSD(T)/II using estimated geometries; see text. [c] DFT/NL, ref 24. [d] Reference 20. [e] Reference 21. [f] Reference 22.

Table 7. Theoretically Predicted First Dissociation Energies (kcal mol^{-1}) at the HF, MP2, and CCSD(T) Level of Theory Using Basis Set II

M	HF[a]	MP2[b]	CCSD(T)[b]
Cr	21.0	58.0	45.8
Mo	26.3	46.1	40.4
W	34.8	54.9	48.0

[a] Using geometries at HF/II. [b] Using geometries at MP2/II.

NL method. The calculated dissociation energies ΔE at CCSD(T)/II are significantly higher than the values predicted at the DFT/NL level of theory (Table 6). As shown above, the difference is caused only to a small degree by the use of frozen geometries for $M(CO)_5$ in the DFT(NL) calculations. Since the optimized geometries of $Mo(CO)_6$ and $W(CO)_6$ at MP2/II are nearly the same as the experimental values used in the DFT studies,[24] and because the energy differences using optimized and frozen geometries for $Mo(CO)_5$ and $W(CO)_5$ are small, the main difference between the ΔE values predicted for these molecules must be due to the methods being used and not the geometries. For $Cr(CO)_6$, however, the difference in the ΔE values may additionally be caused by the different geometries of $Cr(CO)_6$ and $Cr(CO)_5$ used in the theoretical studies. As shown above, the Cr–CO distance calculated at MP2/II is too short (1.861 Å) compared with experiment (1.918 Å). The short Cr–CO bond length could mean that a too high bond energy is calculated at the CCSD(T) level. We calculated the bond energy ΔE at the CCSD(T)/II level using the experimental Cr–CO bopnd length of $Cr(CO)_6$ (Table 3). For $Cr(CO)_5$, we used Cr–CO bond lengths estimated from the experimental structure of $Cr(CO)_6$ and from the differences between the pentacarbonyl and the hexacarbonyl calculated at the MP2/II level (Table 3). That is, the axial Cr–CO distance for $Cr(CO)_5$ was taken to be shorter (1.800 Å) than that in $Cr(CO)_6$ (1.912 Å), but the equatorial Cr–CO bond length was taken to be the same as that in the hexacarbonyl. The other geometrical variables were taken from the optimization at MP2/II. The calculated ΔE value for $Cr(CO)_6$ using the estimated geometries is significantly lower (32.5 kcal/mol) than that using the optimized geometry (45.8 kcal/mol).

The first dissociation energy of $Cr(CO)_6$ has been the subject of other theoretical studies. Sherwood and Hall[41] reported a bond energy of 49.8 kcal/mol calculated at the HF level. In the theoretical study by Barnes et al.[16a] the first CO dissociation energy of $Cr(CO)_6$ was calculated at correlated levels using different methods. The theoretical values for ΔE were 34.8 and 32.2 kcal/mol with different basis sets at the modified coupled-pair functional level (MCPF), 38.8 kcal/mol at CCSD, and 42.7 kcal/mol at CCSD(T) using all-electron wave functions.[16a] The CCSD(T) value reported in this study[16a] (42.7 kcal/mol) is very similar to our result (45.8 kcal/mol).

Table 7 shows the calculated first dissociation energies ΔE at the HF, MP2, and CCSD(T) level of theory using basis set II. It is interesting to note that the trend of the calculated M–CO bond energies predicted at HF/II is close to the experimental values reported from the laser pyrolysis experiments.[22] The absolute values are too low by ~15 kcal/mol, which can be explained by the too long M–CO bonds calculated at the HF level. The ΔE values are higher at MP2/II, particularly for $Cr(CO)_6$. This is due to the shorter M–CO bond lengths calculated at MP2/II. The CCSD(T) values for ΔE are lower than those at MP2, but higher than those at HF (Table 7). It should be noted that $Cr(CO)_6$ is calculated at the HF level to be bound relative to $Cr(CO)_5$ + CO. It has recently been shown that the restricted Hartree–Fock energy of $Cr(CO)_6$ is actually higher than the energy of the ground-state fragments Cr + 6CO.[42]

We studied the effect of a reduced correlation space upon the calculated first dissociation energy. If the $(n-1)$s and $(n-1)$p electrons are frozen in the CCSD(T) calculations, the ΔE values are 42.9 kcal/mol for $Cr(CO)_6$, 38.4 kcal/mol for $Mo(CO)_6$, and 46.0 kcal/mol for $W(CO)_6$. Thus, the correlation of the $(n-1)$s and $(n-1)$p electrons is important for the predicted first dissociation energies of $M(CO)_6$. The differences are 2.9 kcal/mol for $Cr(CO)_6$ and 2.0 kcal/mol for $Mo(CO)_6$ and $W(CO)_6$. We also investigated the effect of adding an additional f-type

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(53) The electronic ground state of Cr and Mo is ^7S with the configuration $(n)s^1(n-1)d^5$.[58] The electronic ground state of W is the ^5D state with the configuration $6s^25d^4$, which is 8.4 kcal/mol lower in energy than the ^7S state.[54] At the CCSD(T)/II level is the ^7S state of W calculated 3.1 kcal/mol lower than the ^5D state. Therefore, we took the calculated total energy for the ^7S state of W for the calculation of the reaction energy of reaction 2.

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Table 8. Theoretically Predicted and Experimentally Observed Total Dissociation Energies (kcal mol^{-1})

M	ΔE	ΔH^{298}	$\Delta E_{calc}{}^a$	$\Delta E_{calc}{}^b$	$\Delta E_{calc}{}^c$	$\Delta E_{calc}{}^d$	$\Delta E_{calc}{}^e$	$\Delta H_{exp}{}^f$	ΔH_{exp}
Cr	140.6	139.6	153.4	109.5	207.6	200	139.4, 136.4	154.9	152.2
Mo	184.5	183.8 (209.8)^h	180.7 (209.1)^h					218.0	217.2
W	239.1	237.8	223.7					255.2	256.0

[a] LDA/NL, ref 24. [b] MCPF, ref 16b. [c] Xα, ref 57c. [d] CISD, ref 50. [e] CCSD(T) using two different basis sets, ref 16a. [f] Reference 47. [g] Reference 51. [h] Calculated using the energy of the ^{1}S state and the experimental excitation energy $^7S \rightarrow {}^1S$ for molybdenum; see text.

polarization function[59] to the metal atom upon the dissociation energies. The calculations at the CCSD(T) level of theory using basis set II+f were only possible with the reduced correlation space without the $(n-1)$s and $(n-1)$p electrons. The first dissociation energy of Cr(CO)$_6$ remained unchanged ($\Delta E = 42.9$ kcal/mol), while the values for Mo(CO)$_6$ ($\Delta E = 38.3$ kcal/mol) and W(CO)$_6$ ($\Delta E = 45.8$ kcal/mol) were slightly smaller. It appears that the additional set of f-type polarization functions has little influence upon the dissociation energies.

We compare now the theoretically predicted dissociation energies at the CCSD(T)/II level with the experimental results. For this we must first convert the bond energies ΔE into bond enthalpies ΔH. The addition of ZPE corrections to ΔE values gives bond enthalpies ΔH^0 at 0 K. Table 6 shows that the calculated ΔH^0 values are $\sim$2 kcal/mol lower than the ΔE values. The thermal corrections at 298° for reaction 1 include the work term $pV = RT$ (0.6 kcal/mol), three degrees of translation ($(3/2)RT = 0.9$ kcal/mol), and two degrees of rotation ($RT = 0.6$ kcal/mol) for 1 mol of CO produced in the reaction. The thermal corrections to the ZPE values were calculated as <0.1 kcal/mol. Combining the thermal corrections with the calculated bond energies gives theoretically predicted ΔH^{298} values which may be compared with the observed results obtained from gas-phase and solution experiments (Table 6).

The most important result given by the comparison of the theoretical and experimental data listed in Table 6 is the excellent agreement of the ΔH^{298} values predicted at the CCSD(T)/II level and the gas-phase values for Mo(CO)$_6$ and W(CO)$_6$. The differences between the experimental and theoretical data are within the experimental error range. This is a very gratifying result, which indicates a theoretical level that might give reliable bond energies for closed-shell transition metal complexes of the second- and third-row transition elements.[43] The lower energy values for Mo(CO)$_6$ and W(CO)$_6$ reported from kinetic studies in solution[20] are most likely due to activation barriers for an associative/dissociative mechanism, which has been reported as the dominant reaction path for the substitution reaction of Mo and W carbonyl complexes.[25] For Cr(CO)$_6$, the experimental values from solution[20,21] and gas-phase[22] experiments are very similar (36–38 kcal/mol). The mechanistic studies show that, unlike molybdenum and tungsten, chromium carbonyl complexes show a dissociative/associate reaction mechanism in substitution reactions.[25] The slightly lower theoretical value predicted at CCSD(T)/II (32.0 kcal/mol) may be caused by using an estimated geometry for Cr(CO)$_5$.

The results indicate that the agreement between the theoretical value calculated at the DFT/NL level[24] and the solution experiment[20,21] for the first dissociation energy of Mo(CO)$_6$ is fortuitous.[46] The conclusion about the order of bond strength in the hexacarbonyls of Cr, Mo, and W based on the DFT/NL results is not justified. The higher reactivity of molybdenum carbonyl complexes than that of chromium analogues in substitution reactions[20] is due to a change in the mechanism of the reaction, rather than a weaker M–CO bond. The theoretical results presented here and the experimental values obtained from gas-phase experiments[22] are strong evidence that the first dissociation energy of the metal hexacarbonyls M(CO)$_6$ shows the order Cr < Mo < W. The theoretical and experimental data suggest the following values for ΔH^{298}: Cr(CO)$_6$ = 37 ± 2 kcal/mol; Mo(CO)$_6$ = 40 ± 2 kcal/mol; W = 46 ± 2 kcal/mol.[60]

We calculated also the *total* bond energies of the hexacarbonyls dissociating into the metal atom in its ground state and six molecules of CO:

$$M(CO)_6 \rightarrow M + 6CO \qquad (2)$$

Experimental values for the dissociation reaction 2 are available[47–49] and may be compared with the theoretical results shown in Table 8.

The total dissociation energy of Cr(CO)$_6$ predicted here (139.6 kcal/mol) is 12–14 kcal/mol lower than the experimental value. Nearly the same theoretical results are reported by Barnes et al.[16a] using the CCSD(T) approximation with all-electron basis sets (Table 8). This is further evidence that ECP methods give results comparable to all-electron wave functions.[5] The total bond energies calculated at CISD[50] and at the X$_\alpha$ level[57c] are too high. The LDA/NL results reported by Ziegler et al.[24] show a much better agreement with experiment for Cr(CO)$_6$. For Mo(CO)$_6$ and W(CO)$_6$, however, the CCSD(T) results[61] for the total bond energies are in better agreement with the experimental values than the LDA/NL data. Still, the difference between theory and experiment is larger for Mo(CO)$_6$ and W(CO)$_6$ than that for Cr(CO)$_6$. In particular the theoretically predicted total bond energy for Mo(CO)$_6$ (183.8 kcal/mol) shows a significant error. Part of this error can be explained by the calculated energy of the metal atom. Reaction 2 is not isogyric,[51] because the metal atom is calculated in the ^{7}S ground state.[52,53] We calculated Mo in the lowest singlet state, the ^{1}S state with the configuration 5s^{2}4d^4. The calculated excitation energy $^7S \rightarrow {}^1S$ for Mo at CCSD(T)/II is 95.3 kcal/mol; the experimental value is 70.0 kcal/mol.[54] The calculated reaction energy for reaction 1 yielding (^{1}S) Mo combined with the experimental excitation energy $^7S \rightarrow {}^1S$ for Mo (70.0 kcal/mol)[54] gives $\Delta H^{298} = 209.1$ kcal/mol for the total bond energy of Mo(CO)$_6$, which is in much better agreement with the experimental value of $\sim$218 kcal/mol.[47,48] It seems that calculated energies for isogyric reactions combined with experimental excitation energies give more accurate results for reaction 2. Unfortunately, we could not find experimental values for the $^7S \rightarrow {}^1S$ excitation energies of Cr and W.

5. Summary

The theoretical results reported here demonstrate that the calculation of compounds of the first row of the transition metals appears to be more difficult than that of molecules of the second- and third-row elements.[55] The M–CO bond lengths of (O_h) Mo(CO)$_6$ and W(CO)$_6$ are predicted in excellent agreement with experiment at the MP2/II level, but the calculated Cr–CO bond is too short. Also, the first CO dissociation energy calculated at

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[60] As one referee pointed out, an activation barrier for CO loss from Cr(CO)$_6$ $E_a = 45$ kcal/mol is reported in ref 22, which appears to be in good agreement with the calculated value at the CCSD(T)/II level of theory (45.8 kcal/mol). However, as pointed out in ref 22, the CO dissociation reaction of Cr(CO)$_6$ is more complex than that of the other carbonyls. It involves subsequent dissociation of CO from other Cr(CO)$_n$ species. If this is taken into account, the dissociation energy for loss of one CO becomes 36.8 kcal/mol.[22] The agreement of the calculated value (45.8 kcal/mol) and the activation barrier (45 kcal/mol) is probably fortuitous.

[61] A detailed analysis of the coupled cluster methods has been given: He, Z.; Cremer, D. *Theor. Chim. Acta* **1993**, *85*, 305.

CCSD(T)/II using MP2-optimized geometries is in good agreement with experimental results obtained from gas-phase laser pyrolysis,[22] while the theoretical value for $Cr(CO)_6$ is too high. The disagreement between the theoretical and experimental dissociation energy for $Cr(CO)_6$ appears to be mainly due to the calculated geometries. A much lower dissociation energy is predicted at the CCSD(T) level when the experimental Cr–CO bond length is used for $Cr(CO)_6$ and an estimated Cr–CO distance for $Cr(CO)_5$. The theoretical values for the dissociation energies of $Mo(CO)_6$ and $W(CO)_6$ indicate that the energies obtained from kinetic studies of substitution reactions[20] refer to a different mechanism of the reaction, which has been shown by recent experimental investigations.[25] The agreement between the calculated dissociation energies using DFT techniques[24] and the values reported from the kinetic studies[20] is probably fortuitous and should not be taken as evidence for the relative M–CO bond energies of the hexacarbonyls of Cr, Mo, and W. The total binding energy between the metal atom and the carbonyl ligands in $M(CO)_6$ is calculated with slightly lower values than experiment. The metal ligand bond energies are predicted in much better agreement with experiment when isogyric reactions are used and the calculated results are combined with experimental excitation energies of the atoms.

Note Added in Proof: Prof. Ziegler has informed us that he recalculated the first dissociation energies of $M(CO)_6$ (M = Cr, Mo, W) using density functional theory with inclusion of nonlocal corrections and relativistic effects. His latest results for $Mo(CO)_6$ (39.7 kcal/mol) and $W(CO)_6$ (43.7 kcal/mol) are in agreement now with our values and with the experimental gas-phase data. Ziegler's calculated result for $Cr(CO)_6$ (46.2 kcal/mol) is higher than the experimental gas-phase value, but close to our CCSD(T) result of 45.8 kcal/mol. We thank Prof. Ziegler for sending us a preprint of his work: Li, J.; Schreckenbach, G.; Ziegler, T. *J. Phys. Chem.*, submitted for publication.

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