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Theoretical studies of the transition metal–carbonyl systems MCO and M(CO)₂, M = Ti, Sc, and V

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Ab initio calculations on the transition metal–carbonyl systems MCO and M(CO)₂, M = Ti, Sc, and V, have been carried out using large Gaussian basis sets and an extensive treatment of electron correlation. The dissociation energies (D_e) and geometries of these molecules are given, and the bonding mechanisms are discussed. High-spin ground states are favored for the monocarbonyl molecules, whereas for the dicarbonyl molecules there is a competition between high-, intermediate-, and low-spin states, which are found to be very close in energy. The computed D_e (Ti–CO) is 0.62 eV whereas for Ti(CO)₂ it is 1.02 eV, relative to the ground state Ti atomic asymptote and CO($^1\Sigma^+$). This suggests that the recent experiment giving a value of ≈ 1.75 eV for D_e [Ti–(CO)$_x$] should be interpreted as giving the D_e for Ti(CO)$_x$, $x \geqslant 2$. For the three metal atoms the binding energy per carbonyl is found to be significantly lower for the dicarbonyl than the monocarbonyl molecules. This is in contrast to the Ni(CO)$_x$ molecules, where each CO is bound with approximately the same energy.

I. INTRODUCTION

Transition metal complexes have been the focus of continued study, both theoretically and experimentally, because of the important role of metal–CO bonding in catalytic processes.[1] The simplest example of these complexes is the M–CO molecule, which is considered to be a prototype for the metal surface–CO interaction. The strength of the M–CO bond has direct relevance to the metal surface–CO interaction, and a qualitative understanding of how this varies for different metals is desirable. The M(CO)$_x$ systems are also of importance in organometallic chemistry and heterogeneous catalysis,[1] and again the strength of the M–CO bond is important. The M–CO binding energies can be computed accurately using *ab initio* techniques, and qualitative understanding of the bonding mechanisms may also be found from these calculations.

In general, the published work on metal–carbonyl systems has concentrated on the right-hand side of the first transition row, with a very large number of papers published on NiCO.[2,3] However, for the systems from the left-hand side of the first transition row the theoretical and experimental information is quite sparse. Theoretically, TiCO has been studied at the self-consistent field/generalized valence bond (SCF/GVB) level in a minimal basis,[4] and ScCO has been studied using the singles and doubles configuration interaction (SDCI) technique.[5] Experimentally, there has been a recent determination of the binding energy of Ti–(CO)$_x$ as ≈ 1.75 eV.[6] We note that the same spectroscopic technique, but with a different method of preparing the metal carbonyl complex, gave a lower bound to the binding energy for NiCO of ≈ 1.10 eV.[6] This is in good agreement with a previous experimental D_e (Ni–CO) of 1.26 ± 0.65 eV[7] and *ab initio* results for NiCO, the most recent of which gives D_e (Ni–CO) as 1.30 eV.[3] There is also some matrix infrared absorption data for ScCO[2] and V(CO)$_x$, $x = 1,5$,[8] and some matrix ESR studies of V(CO)$_x$, $x = 1,3$.[9]

In this paper we present *ab initio* electronic structure calculations on the systems MCO and M(CO)₂, M = Ti, Sc,

and V, including electron correlation at a high level of treatment. We consider the ground state and several low-lying excited states in each case. The calculated D_e for TiCO and Ti(CO)₂ is compared with the Ti(CO)$_x$ binding energy determined from experiment, and the probable number (x) of CO molecules present in the experimentally observed complexes is discussed. Vibrational frequency shifts are calculated for the monocarbonyl complexes, and compared with the available experimental data. The qualitative nature of the bonding in these systems is also discussed in some detail. Finally, the bonding of CO to transition metal atoms from the left-hand side of the first transition row is compared and contrasted to the Ni(CO)$_x$ molecules, a typical system from the right-hand side of the first transition row.

II. METHODS

In this section we consider first the 1-electron basis sets, and then consider the treatment of the n-electron problem.

For all the systems we use basis sets derived from the (14s9p5d) transition-metal sets of Wachters[10] and the (9s5p) C and O sets of van Duijneveldt.[11] The (14s9p5d) metal basis sets are contracted to [8s4p3d] using Wachters contraction 2. This is supplemented with two diffuse 2p functions (0.152 340 and 0.051 080 for Ti, 0.134 620 and 0.046 548 for Sc, and 0.166 872 and 0.054 567 for V) based on those optimized by Wachters for the $3d^n 4s^1 4p^1$ occupation, and the diffuse 3d function of Hay.[12] This yields final metal basis sets of (14s11p6d) functions, contracted to [8s6p4d]. The C and O basis sets are contracted to [4s3p] based on a (5211) contraction of the s space, and a (311) contraction of the p space. To study the importance of 3s3p correlation in these systems, we use a second basis set in which the metal p space is more flexibly contracted as (4211111). This gives a (14s11p6d)/[8s7p4d] metal basis set when 3s3p correlation is included.

For TiCO, we also use a larger basis derived from the (21s13p8d) basis set optimized by Partridge[13] for the $^3F(3d^2 4s^2)$ state of Ti. Three even-tempered 2p functions are

added to describe the $4p$ orbital and two even-tempered diffuse $3d$ functions are added to describe the $^5F(3d^34s^1)$ and $^5D(3d^4)$ states. Six even-tempered $4f$ polarization functions, of the form $\alpha = 2.5^n \times 0.0557$, $n = 0,...5$, are also added. This large primitive set is contracted using the atomic natural orbital (ANO) procedure,[14] based upon the average of the $^3F(3d^24s^2)$, $^5F(3d^34s^1)$, and $^5D(3d^4)$ states of Ti. To accurately describe the polarizability of Ti, the most diffuse s, p, and d functions are left uncontracted[15]; all the remaining orbitals are the ANOs. Our final Ti ANO basis set is $(21s16p10d\,6f)/[6s4p3d\,2f]$. The C and O basis sets are $(13s8p6d\,4f)/[4s3p2d\,1f]$, contracted using the ANO scheme, as described previously.[16]

For our treatment of the n-electron problem, we use several methods: lower levels of treatment are used to treat many states, and higher levels of treatment are used to study accurately the ground or lowest lying states. Recently, Blomberg et al.[17] found that for neutral NiCO, it was necessary to correlate all of the CO valence electrons, as well as the Ni $3d$ and $4s$ electrons, in order to calculate D_e (Ni–CO) accurately. Blomberg et al. used the modified coupled-pair functional (MCPF) method,[18] and found good agreement between the calculated D_e (Ni–CO) from the MCPF treatment and multireference based treatments, which were 1.30 and 1.43 eV, respectively. This is also in good agreement with the somewhat uncertain experimental result of 1.26 ± 0.65 eV,[7] and the recent determination of ≈ 1.10 eV.[6] The MCPF method has been used successfully to study the neutral and positively charged transition metal hydrides,[19,20] and has also been used to interpret the photodetachment spectrum of NiCO$^-$.[3] In the current work we use the MCPF method to determine accurate D_e values of the MCO and $M(CO)_2$ molecules in a selected number of cases, correlating all the metal and CO valence electrons. Since $3s3p$ correlation is known to affect the atomic term separations for the transition-metal atoms on the left-hand side of the first transition row,[21] we also use the MCPF method to study the effect of $3s3p$ correlation in the MCO and $M(CO)_2$ molecules. We note that when correlating a large number of electrons, it is desirable to have a size-consistent approach, such as the MCPF method, in order to accurately calculate D_e.

The MCPF method is based on a single reference configuration, and is only applicable in a limited number of cases. For electronic states with multireference character, we therefore use a complete active space self-consistent-field (CASSCF) plus multireference SDCI (MRCI) approach. However, correlating all of the valence electrons in the present systems is very difficult with this approach. To explore the electronic structure of the low-lying states in the MCO and $M(CO)_2$ systems, and to calibrate the single-reference MCPF results, we correlate only the metal $3d$ and $4s$ electrons. As much of the breakdown of the single-reference approach occurs because of mixing of the different metal asymptotes, only correlating the metal electrons in the CASSCF/MRCI method should provide a useful calibration. The MRCI calculations correlating only the nominally metal $3d$ and $4s$ electrons consist of all single and double excitations from all of the configurations in the CASSCF

wave function. The importance of higher than double excitations is estimated using the multireference analog of the Davidson correction[22,23] which is denoted $+ Q$.

For the $M(CO)_2$ molecules, there are several states which are close in energy, some of which are very multiconfigurational in character. To determine more reliably the ground state in these cases, we use a more extensive CASSCF/MRCI treatment. We take a selected number of occupations from the CASSCF/MRCI calculations described above, and use these as references in a MRCI calculation correlating the metal $3d$ and $4s$ electrons, and the CO 5σ and 1π electrons, including all spin couplings of the reference occupations in the reference space. This treatment includes the most important electrons for an accurate description of the M–CO interaction, although it does not explicitly include in the reference space any multiconfigurational character arising from the CO electrons. However, these are relatively small effects compared to those arising from the metal, so the current treatment should reliably predict the ordering of the low-lying states in these systems, as well as providing an additional calibration of the MCPF method. We note that all the CASSCF/MRCI D_e values presented here are calculated using a supermolecule approach in order to reduce size consistency errors. Except where noted, the calculations are carried out in either C_{2v} symmetry for the monocarbonyls, or D_{2h} symmetry for the dicarbonyls. However, full $C_{\infty v}$ or $D_{\infty h}$ symmetry is maintained for the SCF and CASSCF calculations on the linear MCO and $M(CO)_2$ systems.

All of our computed D_e values are for the process $M(CO)_x \rightarrow M + xCO$. The zero point correction for such a process is expected to be very small, since the M–C vibrational frequency is only a few hundred wave numbers, and the increase in the C–O vibrational frequency upon dissociation, which is of the same order, will cancel this to some extent. Thus, we compare our computed D_e values directly with the experimental binding energies.

The number of electrons correlated in the current series of molecules varies from 3 in the smallest case up to 33 in the largest case. Table I lists the electrons which are correlated in the different cases, and the numbers in this table will be used throughout the paper when referring to the different calculations. For example, a calculation correlating only the Ti $3d$ and $4s$ electrons in TiCO will be referred to as a Ti-CO($4e$) calculation.

TABLE I. Summary of the number of electrons correlated in the MCO and $M(CO)_2$ calculations.

Metal	CO	Sc	Ti	V
$3d\,4s$	$\cdots$	3	4	5
$3d\,4s$	$3\sigma^24\sigma^25\sigma^21\pi^4$	13	14	15
$3s3p3d\,4s$	$3\sigma^24\sigma^25\sigma^21\pi^4$	21	22	23

Metal	$(CO)_2$	Sc	Ti	V
$3d\,4s$	$(5\sigma^21\pi^4)_2$	15	16	17
$3d\,4s$	$(3\sigma^24\sigma^25\sigma^21\pi^4)_2$	23	24	25
$3s3p3d\,4s$	$(3\sigma^24\sigma^25\sigma^21\pi^4)_2$	31	32	33

The calculations have been performed on the NASA Ames CRAY X-MP/48 and CDC Cyber 205 computers, and the NAS CRAY-2 computers, using the MOLECULE-SWEDEN[24,25] program system, and the MCPF program of Blomberg and Siegbahn.[26]

III. RESULTS AND DISCUSSION

The bonding in the $M(CO)_x$ systems is dative in character, and so is characterized by a simple donor–acceptor mechanism. The strength of the M–CO bond is determined by a balance between π donation from the metal to the CO $2\pi^*$ orbital, and repulsion between the metal σ electrons and the CO 5σ lone pair. In general, there are several mechanisms which may reduce the repulsive interactions, including $4s-4p_\sigma$ hybridization, $4s-3d_\sigma$ hybridization and $4s$ to $3d$ promotion.[27] The low-lying states of these molecules can thus be most easily understood by considering the low-lying states of the metal atom and the $^1\Sigma^+$ ground state of CO, considering such factors as the number of metal π electrons available for back donation, the repulsion in the σ space, and the promotion energy required to achieve the atomic configuration necessary for bonding. In general, states derived from the $3d^n 4s^2$ atomic asymptote are expected to be repulsive, due to the large repulsion between the $4s$ and 5σ electrons.

The bonding in the monocarbonyls and dicarbonyls is similar to the extent that it involves $3d_\pi$ to $2\pi^*$ back donation and $4s-5\sigma$ repulsion in both cases. However, the effect of the repulsive interactions is quite different. In the monocarbonyls, the metal $4s$ orbital may polarize away from the CO 5σ orbital via $4s-4p_\sigma$ hybridization, regardless of the spin coupling. For the high-spin states, $4s-3d_\sigma$ hybridization is not possible and $4s$ to $3d$ promotion is favored, whereas in the lower spin states both mechanisms can be used. As we shall see below, the monocarbonyl complexes have high-spin ground states, using mainly $4s-4p_\sigma$ hybridization to reduce repulsion while maintaining a large exchange energy stabilization.

In the dicarbonyl complexes there is a 5σ lone pair on either side of the metal, $4s-4p_\sigma$ hybridization is unfavorable, and again we cannot have $4s-3d_\sigma$ hybridization and a high-spin coupling. Promotion from the diffuse $4s$ orbital to the more compact $3d$ shell is possible, however, and much more favored than in the monocarbonyl complexes. On the other hand, this is not as efficient a mechanism for reducing the repulsion as $4s-4p_\sigma$ hybridization in the monocarbonyl complexes. Thus, in the dicarbonyl high-spin states, the repulsive forces necessitate a greater M–C bond length, which in turn reduces the effectiveness of the $3d_\pi$ to $2\pi^*$ back donation. Thus, the high-spin states are less favored in the dicarbonyls compared to the monocarbonyls, resulting in a smaller D_e per CO molecule in the high-spin dicarbonyl states compared to the monocarbonyls.

The intermediate- and low-spin dicarbonyl states are more favored in several respects. They may use $4s-3d_\sigma$ hybridization to reduce the repulsive interactions. Also, a lower spin state allows more electrons into the $3d_\pi$ orbitals, and so more $3d_\pi$ to $2\pi^*$ back donation. This is a very important effect, as there are now two CO molecules which can accept

electrons from the metal. Thus, configurations such as $\sigma^1\pi^{n+1}$, $\delta^1\pi^{n+1}$ or even π^{n+2} become much more favored, but require a shorter M–C bond length in order to be strongly bound. The nominally $3d^{n+2}$ type configurations may achieve this easily, whereas the $3d^{n+1} 4s^1$ configuration must make effective use of hybridization or promotion to reduce the $4s-5\sigma$ repulsion. Finally, the presence of two CO molecules also favors the participation of the metal $4p_\pi$ orbitals, as these may donate charge to the π_u combination of the CO $2\pi^*$ orbitals. This donation may occur via $4s$ to $4p_\pi$ promotion on the metal atom, for example.

Counterbalancing these favorable effects is the loss of exchange energy in the lower spin states, and the fact that they may correlate in general with a mixture of high-lying atomic asymptotes, and so require a greater atomic promotion energy to achieve the bonding configuration. Thus, the situation is much more complex than for the monocarbonyls, and this is reflected in the calculations, where a higher level of theory is needed to adequately describe the various states with very different configurational character.

We now move on to a more specific discussion of the results. For reference purposes, the relevant results for free CO in both basis sets are given in Table II. Most of the errors in the SCF treatment of CO are corrected at the $6e$ level, correlating only the CO 5σ and 1π electrons, and the MCPF results are in good agreement with experiment in either basis set. In the following sections we discuss TiCO first, in view of the recent experimental data on the binding energy of the $Ti(CO)_x$ systems. We then discuss ScCO and VCO, comparing and contrasting with the TiCO results. The dicarbonyls are then presented, followed by a comparison with the available experimental data. Finally, a comparison is made between the present systems and the $Ni(CO)_x$ molecules.

A. TiCO

The Ti atom has a $3d^2 4s^2 (^3F)$ ground state, with the $3d^3 4s^1 (^5F)$ and $3d^2 4s^2 (^1D)$ states lying 0.78 and 0.87 eV higher in energy, respectively.[28] The $3d^3 4s^1 (^3F)$ state and lowest $3d^3 4s^1$ singlet state (^1G) lie 1.42 and 2.24 eV above the ground state, respectively.[28] The $3d^3 4s^1$ metal configurations are more favored for bonding to CO than the $3d^2 4s^2$ configuration, as there is less σ repulsion and the possibility of more π back donation with the additional $3d$ electron. However, the $3d^3 4s^1$ state requires a substantial promotion

TABLE II. Summary of the free CO results.[a]

	r_e	μ
$(9s\ 5p)/[4s\ 3p]$ basis set		
SCF	2.120	−0.200
MCPF($6e$)	2.172	0.054
MCPF($10e$)	2.187	0.049
ANO basis set		
MCPF($10e$)	2.139	0.108
Expt. (CO)[b]	2.132	0.048

[a] Bond lengths are in a_0 and dipole moments in a.u.
[b] Huber and Herzberg, Ref. 32.

energy for bonding, as noted above, and energetically this favors the $3d^24s^2$ states. Since there are several low-lying molecular states which may be derived from these atomic states, we consider several singlet, triplet, and quintet states of TiCO at the CASSCF/MRCI level of treatment.

The ordering of several low-lying states of TiCO is given in Table III. These calculations are at the CASSCF/MRCI level, correlating the four nominally metal $3d$ and $4s$ electrons. The geometries are optimized for the lowest three bound states, the $^5\Delta$, $^3\Delta$, and $^5\Pi$. The $^3\Phi$ state is unbound at this level of treatment, dissociating to Ti $3d^24s^2(^3F)$ and CO($^1\Sigma^+$). The energies are relative to the $^5\Delta$ state, which is the ground state at this level of approximation. The $^5\Delta$ state correlates directly with the atomic $3d^34s^1(^5F)$ state of Ti and the $^1\Sigma^+$ state of CO, and the $^3\Delta$ state correlates with the $3d^34s^1(^3F)$ state of Ti. We note that these results are inconsistent with those of Mortola and Goddard,[4] who predicted a $^3\Phi$ ground state for TiCO using SCF/GVB calculations with a minimal basis. However, we feel that the current calculations, with a much larger basis set and more extensive treatment of electron correlation, are more reliable.

Also given in Table III are the CASSCF active spaces and the dominant occupations in the CASSCF/MRCI wave function. The active spaces are designed so that more than 95% of the MRCI wave function is in the CASSCF reference space in all cases. Apart from the $^5\Delta$ state, the states are very multiconfigurational in character. For example, in the $^3\Delta$ state there are three spin couplings of the dominant occupa-

TABLE III. Summary of the MCO CASSCF/MRCI state orderings.[a]

State	Occupation	Active space[b]	ΔE_{CAS}	ΔE_{CI}
TiCO(4e)				
$^5\Delta$	$\sigma^1\delta^1\pi^2$	4222	0.00	0.00
$^3\Delta$	$\sigma^1\delta^1\pi^2$	4222	0.60	0.45
$^3\Phi$[c,d]	$\sigma^2\delta^1\pi^1$	4442	0.58	0.53
$^5\Pi$	$\sigma^1\delta^2\pi^1,\sigma^1\pi^2\pi^1,\sigma^1\sigma'^1\delta^1\pi^1$	5442	0.65	0.72
$^1\Pi$[d]	$\sigma^1\pi^3$	4442	0.83	0.89
$^1\Gamma$[d,e]	$\sigma^1\delta^1\pi^2$	4222	1.04	0.95
ScCO(3e)				
$^4\Sigma^-$	$\sigma^1\pi^2$	2220	0.00	0.00
$^4\Phi$	$\sigma'^1\delta^1\pi^1$	4222	0.31	0.34
$^4\Pi$	$\sigma^1\delta^1\pi^1$	4222	0.44	0.46
VCO(5e)				
$^6\Sigma^+$	$\sigma^1\delta^2\pi^2$	4332	0.00	0.00
$^6\Delta$	$\sigma^1\sigma'^1\delta^1\pi^2$	5332	0.29	0.26
$^4\Delta$[f]	$\sigma^2\delta^1\pi^2$	5332	0.34	0.28
$^4\Pi$	$\sigma^1\delta^1\pi^3$	4332	0.57	0.57
$^4\Phi$	$\sigma^1\delta^1\pi^3$	4332	0.56	0.60

[a] Energy differences are in eV. Except where indicated, the bond lengths are the optimal geometries given in Table IV.
[b] The notation refers to the number of active orbitals in the $a_1,b_1,b_2,$ and a_2 irreducible representations in C_{2v} symmetry.
[c] The $^3\Phi$ state of TiCO is unbound.
[d] The bond lengths for these states are not optimized; r(Ti–C) is 3.95 a_0, r(C–O) is 2.177 a_0.
[e] The $^1\Delta(\sigma^1\delta^1\pi^2)$ state is 0.04 eV higher than the $^1\Gamma$ state at the CASSCF level of calculation.
[f] The $^4\Delta$ state of VCO is unbound. The bond lengths for this calculation are r(V–C) = 3.957 a_0, r(C–O) = 2.159 a_0.

tion which contribute substantially to the wave function, and for the $^5\Pi$ state there are six CSFs with coefficients larger than 0.20. The singlet states are quite high in energy, reflecting the fact that the lowest Ti $3d^34s^1$ singlet states are more than 2.2 eV above the ground state.

The optimal geometry, dipole moments, and Mulliken populations of the lowest three bound states of TiCO from Table III are given in Table IV. In all cases the C–O bond length increases relative to the SCF bond length, due to charge donation into the CO $2\pi^*$ orbital, which is antibonding in free CO. The bond lengths are quite similar for the $^5\Delta$ and $^3\Delta$ states, which may be expected since these states differ only in spin coupling of the open-shell orbitals on Ti. The $^5\Pi$ state has a much larger Ti–C bond length, and a shorter C–O bond length, compared to the $^5\Delta$ and $^3\Delta$ states. This may be understood by considering the bonding mechanism involved. The $^5\Pi$ state bonds through a mixture of $3d_\pi$ to $2\pi^*$ and $4p_\pi$ to $2\pi^*$ donation, giving two important π orbitals to be included in the CASSCF active space, and leading to a large $4p_\pi$ population. Since the $4p$ orbital is diffuse, a greater Ti–C bond length is required for efficient $4p_\pi$ to $2\pi^*$ back donation. However, this reduces the efficiency of the $3d_\pi$ back donation, so the final bond length is a compromise between the optimum bond length for each case. The result is smaller π back donation for the $^5\Pi$ state, as is shown by the lower $2\pi^*$ population. This results in a shorter C–O bond length and a weaker Ti–C bond. We note that the $^3\Delta$ state has a larger $2\pi^*$ population than the $^5\Delta$ state, and yet lies higher in energy, because the Ti $3d^34s^1(^3F)$ state is 0.64 eV above the $3d^34s^1(^5F)$ state. Similarly, the $^5\Pi$ state has a much larger total $4p$ population than the other states, and so is destabilized since the lowest Ti $3d^24s^14p^1$ state is 1.20 eV above the $3d^34s^1(^5F)$ state.

The dipole moments, coupled with the $4p_\sigma$ populations of Table IV, lead to further insight into the bonding mechanisms in these states. The $4p_\sigma$ populations reflect the $4s$–$4p_\sigma$ hybridization, which reduces the repulsion with the CO 5σ lone pair. The $^3\Delta$ state has a larger $4p_\sigma$ population than the $^5\Delta$ state. The larger shift of charge away from the 5σ lone pair in the $^3\Delta$ state results in a dipole moment that is smaller in magnitude than that of the $^5\Delta$ state. For the $^5\Pi$ state, the large change in dipole moment between the CASSCF and MRCI wave functions reflects the difficulty in describing this state at the CASSCF level, even with a large active space. There is a shift in charge from the π to the σ space in going from the CASSCF to the MRCI wave function. In the σ space, the most important orbital is a $4s$–$4p_\sigma$ hybrid, but there is also an important contribution from an orbital which is a mixture of $4s$, $4p_\sigma$, and $3d_\sigma$. The occupation of this orbital is 0.08 in the CASSCF wave function, compared to 0.28 in the MRCI wave function. This large change in occupation represents only a small energetic effect, however, due to a fine balance between nearly degenerate effects in the $^5\Pi$ state: reducing repulsion via $4s$–$3d_\sigma$ and $4s$–$4p_\sigma$ hybridization, and increasing bonding through $3d$ to $2\pi^*$ back donation.

The 4e CASSCF/MRCI results give a qualitative understanding of the electronic structure of TiCO. However, for a more quantitative calculation of properties such as D_e

TABLE IV. Summary of the MCO CASSCF/MRCI geometries and properties.[a]

State	r(M–C)	r(C–O)	μ^b	$3d$	$4s$	$4p_\sigma$	$4p_\pi$	$2\pi^*$
TiCO($4e$)								
$^5\Delta$(CASSCF)	3.976	2.184	− 1.22	2.55	0.88	0.21	0.08	0.52
$^5\Delta$(MRCI)	3.990	2.183	− 1.26	2.54	0.88	0.20	0.10	0.52
$^3\Delta$(CASSCF)	3.962	2.190	− 0.79	2.44	0.84	0.31	0.08	0.59
$^3\Delta$(MRCI)	3.987	2.184	− 0.84	2.47	0.84	0.28	0.11	0.55
$^5\Pi$(CASSCF)	4.203	2.178	− 1.16	2.36	0.87	0.17	0.34	0.47
$^5\Pi$(MRCI)	4.279	2.163	− 0.66	2.43	0.88	0.21	0.28	0.39
ScCO($3e$)								
$^4\Sigma^-$(CASSCF)	4.062	2.209	− 1.57	1.37	0.88	0.26	0.09	0.66
$^4\Sigma^-$(MRCI)	4.069	2.205	− 1.61	1.37	0.88	0.26	0.09	0.65
$^4\Phi$(CASSCF)	4.287	2.197	− 1.46	1.35	0.89	0.21	0.17	0.59
$^4\Phi$(MRCI)	4.298	2.192	− 1.43	1.35	0.89	0.21	0.20	0.56
$^4\Pi^c$ (CASSCF)	4.287	2.197	− 1.60	1.33	0.89	0.23	0.14	0.65
$^4\Pi^c$ (MRCI)	4.298	2.192	− 1.51	1.34	0.89	0.22	0.17	0.60
VCO($5e$)								
$^6\Sigma^+$(CASSCF)	3.957	2.159	− 0.81	3.84	0.83	0.13	0.05	0.34
$^6\Sigma^+$(MRCI)	3.957	2.159	− 0.87	3.81	0.83	0.13	0.07	0.35
$^6\Delta$(CASSCF)	4.111	2.153	+ 0.16	3.57	0.89	0.32	0.08	0.30
$^6\Delta$(MRCI)	4.126	2.152	+ 0.14	3.56	0.89	0.33	0.08	0.30
$^4\Pi$(CASSCF)	3.794	2.216	− 1.91	3.51	0.84	0.20	0.06	0.70
$^4\Pi^d$ (MRCI)	3.794	2.216	− 1.85	3.53	0.83	0.20	0.10	0.66
$^4\Phi$(CASSCF)	3.794	2.214	− 1.79	3.48	0.86	0.22	0.06	0.69
$^4\Phi^d$ (MRCI)	3.794	2.214	− 1.81	3.52	0.85	0.20	0.08	0.66

[a] Energy differences are in eV, dipole moments are in a.u. and bond lengths are in a_0. Geometries are optimized except where indicated.

[b] A negative dipole moment indicates a polarity of M^+CO^-.

[c] Geometry taken from the $^4\Phi$ state optimizations.

[d] Geometry for these calculations are taken from the optimized CASSCF calculations on the same state.

we must correlate additional electrons. These results, obtained using the MCPF method, are presented in Table V. The optimal geometries, D_e values, dipole moments, and Mulliken populations are given for several different numbers of correlated electrons. We present results for the $^5\Delta$ state of TiCO, which is the ground state. For comparison we also give the $4e$ CASSCF/MRCI results.

To establish the validity of the MCPF calculations on these molecules, we compare the $4e$ MCPF and $4e$ CASSCF/MRCI results. The MRCI calculations are expected to be accurate, within the constraints of a $4e$ treatment, and ideally we would expect close agreement between the MCPF and MRCI results. The $4e$ MCPF D_e value is between the CASSCF and MRCI D_e values, and the agreement with the MRCI result is good. The Ti–C bond length is in error by about 0.05 a_0, and the C–O bond length is in error by less than 0.01 a_0, for the $4e$ MCPF calculation. The dipole moment and Mulliken populations for the $4e$ MCPF calculation are in good agreement with both the CASSCF and MRCI results, although the $3d_\pi$ to $2\pi^*$ back donation is underestimated. Thus, the agreement between the $4e$ MCPF and CASSCF/MRCI calculations is very satisfactory for the $^5\Delta$ state of TiCO.

We now consider the more quantitative results obtained by correlating more electrons on the Ti and CO's. There is a 0.47 eV increase in D_e at the $14e$ level, which includes the

CO valence electrons, and a smaller 0.11 eV increase in D_e at the $22e$ level when Ti $3s3p$ correlation is included. The large increase in D_e from correlating the CO valence electrons is due partly to the improved description of the electrostatic contribution from the CO dipole moment (see Table II), which occurs mainly through changes in the π space. Correlating the 5σ lone pair is also important, because this interacts directly with the Ti atom. There are also significant contributions to D_e from the remaining CO σ electrons, which implies that relaxation effects are important. There is only a small change in the Ti–C bond length at either the $14e$ or $22e$ level, but the C–O bond length increases by 0.07 a_0 at the $14e$ level, parallelling the 0.07 a_0 bond length change in free CO between the SCF and $10e$ MCPF calculations (see Table II). The C–O bond length remains unchanged from the $14e$ to $22e$ level, as may be expected since $3s3p$ correlation is a Ti atomic effect.

Turning now to the dipole moments and Mulliken populations, there is more π backdonation as more electrons are correlated, leading to greater binding and a greater C–O bond length. The dipole moment is reduced in magnitude between the $4e$ and $14e$ treatment, due to a correct description of the CO dipole moment (see Table II) and a net movement of $0.1e$ from the CO to the Ti atom. This occurs even though there is more π backdonation in the $14e$ case, indicating a larger donation of charge in the σ space from the CO to

TABLE V. Comparison of the CASSCF/MRCI and MCPF results for the MCO molecules.[a]

	r(M–C)	r(C–O)	D_e[b]	μ[c]	$3d$	$4s$	$4p_\sigma$	$4p_\pi$	$2\pi^*$
TiCO($^5\Delta$)									
CAS(4e)	3.976	2.184	0.65(−0.13)	−1.22	2.55	0.88	0.21	0.08	0.52
MRCI(4e)	3.990	2.183	0.80(0.02)	−1.26	2.54	0.88	0.20	0.10	0.52
MCPF(4e)	3.941	2.186	0.73(−0.05)	−1.23	2.57	0.86	0.18	0.09	0.47
MCPF(14e)	3.910	2.260	1.20(0.42)	−1.00	2.60	0.90	0.20	0.09	0.56
MCPF(22e)	3.901	2.260	1.31(0.53)	−1.22	2.63	0.90	0.16	0.06	0.59
TiCO($^5\Delta$) ANO basis									
MCPF(14e)	3.855	2.208	1.14(0.36)	−1.04	2.62	0.89	0.17	0.07	0.50
ScCO($^4\Sigma^-$)									
CAS(3e)	4.062	2.209	1.18(−0.25)	−1.57	1.37	0.88	0.26	0.09	0.66
MRCI(3e)	4.069	2.205	1.24(−0.19)	−1.61	1.37	0.88	0.26	0.09	0.65
MCPF(3e)	4.043	2.206	1.22(−0.21)	−1.66	1.40	0.88	0.22	0.12	0.60
MCPF(13e)	4.024	2.281	1.60(0.17)	−1.23	1.45	0.92	0.24	0.11	0.63
MCPF(21e)	3.981	2.284	1.73(0.30)	−1.48	1.52	0.92	0.19	0.08	0.66
VCO($^6\Sigma^+$)									
CAS(5e)	3.957	2.159	0.23(−0.02)	−0.81	3.84	0.83	0.13	0.05	0.34
MRCI(5e)	3.957	2.159	0.35(0.11)	−0.87	3.81	0.83	0.13	0.07	0.35
MCPF(5e)	4.036	2.147	0.26(0.02)	−0.38	3.85	0.85	0.13	0.05	0.25
MCPF(15e)	3.843	2.240	0.77(0.53)	−0.67	3.79	0.86	0.16	0.06	0.45
MCPF(23e)	3.839	2.240	0.89(0.65)	−0.83	3.80	0.86	0.13	0.05	0.48

[a] Bond lengths are in a_0, dissociation energies in eV, and dipole moments in a.u. All geometries are optimized.

[b] Relative to Ti$^5F(3d^34s^1)$, Sc$^4F(3d^24s^1)$, V$^6D(3d^44s^1)$, respectively, and CO $^1\Sigma^+$. The values in parentheses are relative to Ti$^3F(3d^24s^2)$, Sc$^2D(3d^14s^2)$, V$^4F(3d^34s^2)$, respectively, and CO$^1\Sigma^+$, corrected using the experimental $3d^{n+1}4s^1$–$3d^n4s^2$ separation. The CASSCF/MRCI D_e values are computed relative to an M–CO supermolecule [r(M–C) = 100.0 a_0, r(C–O) = 2.12 a_0], in order to reduce size consistency errors.

[c] A negative dipole moment indicates a polarity of M$^+$CO$^-$.

the Ti. Including $3s3p$ correlation gives an increase in the magnitude of the dipole moment. This is due to a slight increase in π backdonation compared to the 14e result, and a small movement of charge from the Ti to the CO. There is also a slight reduction in the $4p_\sigma$ population, and an increase in the $3d$ population. This movement of charge from the $4s$–$4p_\sigma$ hybrid pointing away from the CO to the more compact $3d$ shell also contributes to the increase in the magnitude of the dipole moment for the 22e calculation.

Finally, we note that the 14e results in the large ANO basis are in good agreement with the 14e results in the smaller basis. The larger basis illustrates the effect of polarization functions on the metal and ligand, and is expected to have less superposition error due to the large primitive set. Both bond lengths are slightly shorter in the ANO basis, although much of the change in the C–O bond length may be seen in the free CO results of Table II. The charge distribution is quite similar in either basis, although the backdonation is smaller in the ANO basis. The binding energy is smaller in the ANO basis, which is probably due to the reduced superposition error. Overall, however, the smaller basis set results are quite satisfactory.

The 22e MCPF treatment of TiCO represents our most reliable determination of D_e as 1.31 eV. As seen in Table V, the 4e MCPF D_e is about 10% smaller than the 4e MRCI D_e value, indicating that the true D_e will be larger than 1.31 eV at the 22e level of treatment. However, the ANO basis set results indicate that the small basis set D_e value will be

slightly too large, due to basis set superposition error. Considering both these factors, our best estimate for D_e (Ti–CO) is 1.40 eV, relative to the $3d^34s^1(^5F)$ atomic asymptote.

B. ScCO

The ground state of the Sc atom is $3d^14s^2(^2D)$, with the $3d^24s^1(^4F)$ and $3d^24s^1(^2F)$ states lying 1.427 and 1.846 eV above the ground state, respectively.[28] Jeung and Koutecky[5] have previously studied ScCO at a qualititive level using the SDCI approach, with a double-zeta valence basis and pseudopotentials for the core electrons. They found that the states derived from the atomic ground state and CO($^1\Sigma^+$) were repulsive, which is to be expected due to the filled $4s$ shell. We have found a similar result for TiCO, where the $^3\Phi$ state was found to be unbound. They predicted a $^4\Sigma^-$ ground state for ScCO, derived from the occupation $4s^13d_\pi^13d_\pi^1$ with a $^4\Pi$ state lying about 0.30 eV higher in energy, derived from $4s^13d_\pi^13d_\delta^1$. In the current work we consider these two states, and the $^4\Phi$ state derived from the $4s^13d_\pi^13d_\delta^1$ occupation.

The 3e CASSCF/MRCI results for the $^4\Sigma^-$, $^4\Phi$, and $^4\Pi$ states of ScCO are given in Tables III and IV. The $^4\Phi$ state is below the $^4\Pi$ state, which may be expected from Hund's rules. Both states are dominated by two symmetry-equivalent configurations when treated in C_{2v} symmetry as in the current calculations, and so are not amenable to single refer-

ence techniques such as SDCI or MCPF. Thus, the SCF reference function used by Jeung and Koutecky[5] is probably a linear combination of $^4\Phi$ and $^4\Pi$ states, leading to a symmetry broken SDCI wave function. Nevertheless, the separation found by Jeung and Koutecky between the $^4\Sigma^-$ state and the "$^4\Pi$" state is comparable to the 0.30 eV separation between the $^4\Sigma^-$ state and the $^4\Phi$ state in the current work.

The $^4\Phi$ state has a significantly greater Sc–C bond length than the $^4\Sigma^-$ state, due to the smaller back donation and the larger $4p_\pi$ population in the $^4\Phi$ state. The $^5\Pi$ state of TiCO is somewhat similar in this regard, bonding through a mixture of $3d_\pi$ and $4p_\pi$ to $2\pi^*$ donation. However, the bonding is stronger for ScCO, as indicated by the larger back donation effect. Thus, although the $^4\Phi$ and $^4\Pi$ states have only one nominally $3d_\pi$ electron, they still donate a significant amount of charge to the CO $2\pi^*$ orbital. This implies a donation from the CO to the metal in the σ space, since the total $3d$ population is quite similar to the $^4\Sigma^-$ ground state. Finally, compared with the $^5\Delta$ ground state of TiCO, the $^4\Sigma^-$ state is obtained by removing a (nonbonding) $3d_\delta$ electron, whereas the $^4\Delta$ state is obtained by removing a (bonding) $3d_\pi$ electron. Thus it is not surprising that the $^4\Sigma^-$ state is the ground state for ScCO.

In Table IV we present the MCPF results for the $^4\Sigma^-$ state of ScCO, and for comparison the $3e$ CASSCF/MRCI results. The $3e$ MCPF and $3e$ CASSCF/MRCI results in general agree well. As for TiCO, however, the MCPF method underestimates the $3d_\pi$ to $2\pi^*$ backdonation. Correlating more electrons gives trends similar to TiCO. The dissociation energy increases significantly, and the changes in charge distribution and dipole moment are similar to those found in TiCO. The effect of $3s3p$ correlation on D_e is slightly larger in ScCO than TiCO: 0.13 eV in ScCO compared with 0.09 eV in TiCO. Since $3s3p$ correlation is more important in Sc atom that Ti atom,[21] and the $3s3p$ orbitals are more diffuse,[21] a larger differential effect is expected in ScCO.

Our best estimate for D_e (Sc–CO), taking account of errors in the MCPF calculation and basis set superposition error, is 1.70 eV relative to the $3d^2 4s^1 (^4F)$ atomic asymptote. The net dissociation for ScCO, calculated relative to the $3d^{n+1} 4s^1$ asymptote to which these molecules dissociate, is significantly greater than that for TiCO. This is due to the larger $3d_\pi$ to $2\pi^*$ back donation in ScCO, which is due to several related effects. The $3d$ orbitals are more diffuse in Sc atom than in Ti atom, and the relative size of the $4s$ orbital to the $3d$ orbitals is reduced.[21] Also, the ionization potential for the process $M(3d^{n+1} 4s^1) \rightarrow M^+ (3d^n 4s^1)$ is 24% lower for Sc atom than Ti atom.[28] Thus, the $3d$ orbitals more easily donate charge to the CO in ScCO, and there is less $4s$–5σ repulsion to overcome, giving a larger D_e value.

C. VCO

The ground state of the V atom is $3d^3 4s^2 (^4F)$, with a $3d^4 4s^1 (^6D)$ state lying only 0.32 eV higher in energy, and the lowest lying quartet (^4D) and doublet (^2P) $3d^4 4s^1$ states lying at 1.03 and 2.32 eV, respectively.[28] The energy difference between the atomic ^6D and ^4D states reflects a loss of exchange energy, which also affects the molecular states. Based on the TiCO and ScCO results, the ground state of

VCO is most likely to be derived from the $3d^4 4s^1 (^6D)$ atomic asymptote, whereas the quartet and doublet states are expected to lie somewhat higher in energy. Thus, we only briefly consider the quartet molecular states, and do not consider any doublet states.

The ground state of VCO is calculated to be $^6\Sigma^+$, as shown in Table III. This state correlates with the $3d^4 4s^1 (^6D)$ state of V atom and the $^1\Sigma^+$ state of CO, and is related to the $^5\Delta$ ground state of TiCO by the addition of an electron into a (nonbonding) $3d_\delta$-type orbital, high-spin coupled. Thus, the ground states of all three MCO molecules considered here are simply related in a configurational sense, all being high-spin coupled, and differing only in the number of electrons in (nonbonding) $3d_\delta$-type orbitals.

We note that for the CASSCF treatment of the $^6\Sigma^+$ state of VCO, three active orbitals were necessary in the b_1 and b_2 irreducible representations involving the π electrons, even though only one is strongly occupied in each representation. This indicates that there is an additional correlation effect important in VCO, possibly $3d$–$3d$ correlation, which is not as important in TiCO or ScCO, and which competes energetically with the $3d_\pi$ to $2\pi^*$ backdonation. Thus, more variational flexibility is necessary in the CASSCF active space to allow both effects to be treated in a balanced manner. As noted below, the back donation in VCO is much smaller than in TiCO or ScCO, so that the increased $3d$–$3d$ correlation in V atom may be relatively more important.

There is also a $^6\Delta$ state of VCO derived from the ^6D state of V atom, which lies at 0.26 eV as shown in Table III. This state has a $4s^1 3d_\sigma^1$ occupation in the σ space, and so is less favorable than the $^6\Sigma^+$ state due to the additional σ repulsion. The $^4\Delta$ state is unbound at the current level of treatment, dissociating to V $3d^3 4s^2 (^4F)$ and CO $^1\Sigma^+$. The $^4\Pi$ and $^4\Phi$ states are almost degenerate, lying significantly higher than the $^6\Sigma^+$ ground state. The large π active space used for the ground state was also necessary for a good description of the quartet states.

Table IV gives the geometries and properties of the bound sextet and quartet states of VCO considered here. For the $^6\Sigma^+$ ground state, we see a much reduced backdonation effect compared to TiCO or ScCO, with the $2\pi^*$ population only 54% that of the $^4\Sigma^-$ state of ScCO. The C–O bond length reflects this change, being 0.05 a_0 shorter for VCO than for TiCO or ScCO. The $4p_\sigma$ population is also smaller in VCO, indicating less $4s$–$4p_\sigma$ hybridization, and so more $4s$–5σ repulsion. For the $^6\Delta$ state, the greater M–C bond length and larger $4p_\sigma$ population are due to the additional repulsion from the extra σ electron. These changes in geometry and charge distribution lead to changes in the dipole moment which is quite different from that of the $^6\Sigma^+$ ground state. The $^4\Pi$ and $^4\Phi$ states of VCO have significantly shorter V–C bond lengths and greater C–O bond lengths when compared to the $^6\Sigma^+$ ground state, due to the much larger backdonation in the quartet states, which is also reflected in the dipole moments. As noted previously, the quartet atomic states in V atom lie significantly higher in energy than the sextet state. Thus, even with stronger bonding, the quartet states still lie relatively high in energy.

In Table V we present the MCPF results for the $^6\Sigma^+$

state of the VCO and compare these with the CASSCF/MRCI results. The agreement between the $5e$ MCPF and $5e$ CASSCF/MRCI results is not as good as for the analogous calculations on TiCO and ScCO. The backdonation is smaller in the MCPF wave function, and the C–O bond length reflects this. As well as differing in the π space, there is a rearrangment in the σ space which allows the CASSCF/MRCI wave functions to retain the same overall $3d$ population as the MCPF wave function, but still donate more $3d_\pi$ to the CO. This rearrangment in the σ space, coupled with the π space difference, leads to the large difference in dipole moments between the two calculations.

Interestingly, the $5e$ MCPF D_e calculated relative to the $3d^4 4s^1$ asymptote is slightly larger than the CASSCF D_e, even though the π backdonation is smaller. This is probably an artifact of the supermolecule approach used to calculate the CASSCF D_e, which has the same 4332 active space as the VCO molecule at the equilibrium geometry. This may lead to a description of the V atom in the supermolecule which is slightly better than that at equilibrium, leading to a smaller D_e. This imbalance is corrected at the MRCI level, where the D_e is larger than in the MCPF calculation.

Overall, it seems that the MCPF approach does not describe the $^6\Sigma^+$ state of VCO as well as either the $^5\Delta$ state of TiCO or the $^4\Sigma^-$ state of ScCO. This is probably due to errors in the SCF description of VCO. We have already noted that a larger CASSCF active space was necessary for VCO than TiCO or ScCO, indicating that VCO is somewhat more complicated to describe. Thus it seems that the MCPF method is not able to completely overcome the SCF errors in VCO.

The effect of correlating more electrons for VCO is similar to the effect in TiCO and ScCO. There is an increase in D_e upon correlating the CO valence electrons, and an increase similar in magnitude to Ti upon correlating the $3s3p$ electrons on V. Again there is more π backdonation as more electrons are correlated, leading to a larger dissociation energy, and changes in the dipole moment.

Our best estimate for D_e (V–CO) is 1.15 eV, relative to the $3d^4 4s^1 (^6D)$ atomic asymptote. VCO is more weakly bound than either TiCO or ScCO. The $3d$ orbitals are more contracted in V atom than Ti and Sc atoms, and the relative size of the $4s$ orbital to the $3d$ orbitals is greater.[21] There is less $4s–4p_\sigma$ hybridization in VCO, which leads to a larger repulsion. Also the ionization potential for the process $M(3d^{n+1}4s^1) \rightarrow M^+(3d^n 4s^1)$ is slightly (7%) higher for V than Ti.[28] The overall effect is less $3d_\pi$ backdonation, less hybridization, and more repulsion, giving a smaller binding energy.

D. Ti(CO)$_2$

The ordering of the low-lying quintet, triplet, and singlet states for Ti(CO)$_2$ is given in Table VI. As for TiCO, these results are from CASSCF/MRCI calculations, correlating only the four nominally $3d$ and $4s$ electrons. Also given in Table VI are the CASSCF active spaces, and the dominant occupations in the CASSCF/MRCI wave functions. The ground state is $^5\Delta_g$, derived directly from the $^5\Delta$ ground

state of TiCO. In contrast to TiCO, however, the excited states are much lower in energy, the $^3\Pi_g$ and $^1\Sigma_g^+$ states being almost degenerate with the ground state. Apart from the high-spin $^5\Delta_g$ state, there is little similarity between the configurational character of the low-lying states of TiCO and those of Ti(CO)$_2$, an observation which also applies to the Sc and V systems. There is a much more important effect from configurations with π^3 character, these being nominally three $3d_\pi$ electrons (π_g^3) or two $3d_\pi$ electrons and one $4p_\pi$ electron ($\pi_g^2 \pi_u^1$), which then donate charge to the CO $2\pi^*$ orbitals. The fourth electron is in either a σ or δ orbital. Thus, although the σ orbital is favored through the lower energy of the $3d^3 4s^1$ atomic configuration compared to the $3d^4$ configuration [the lowest of which is 2.77 eV above the Ti $3d^3 4s^1 (^5F)$ state], the δ orbital, with its lower repulsion, becomes more important when two CO molecules are present. The $^1\Sigma_g^+$ state, nominally $3d^4$ in character, is remarkably low in energy. However, as discussed below, there is so much backdonation associated with this state that it is somewhat misleading to describe it as $3d^4$. As for TiCO, the states are in general very multiconfigurational, requiring large CASSCF active spaces for an adequate description.

The optimal geometry, dipole moments, and Mulliken populations of the lowest five states of Ti(CO)$_2$ are given in Table VII. The $^3\Gamma_g$ state is unbound at the CASSCF level, and at the MRCI level has only a very shallow minimum in the potential curve for the Ti–C bond coordinate due to a curve crossing with the $3d^2 4s^2 (^3F)$ atomic asymptote. Thus, it is not included in Table VII. the C–O bond lengths for Ti(CO)$_2$ follow similar trends to those found for the monocarbonyls as they are highly correlated with the $2\pi^*$ populations. For the $^5\Delta_g$ state, the total $3d_\pi$ to $2\pi^*$ donation is only slightly more than in the $^5\Delta$ state of TiCO, so that the net donation per CO molecule is much less. The Ti–CO bond is much weaker and the C–O bond is stronger, leading to a greater Ti–C bond length and a shorter C–O bond length for Ti(CO)$_2(^5\Delta_g)$ as compared to TiCO($^5\Delta$). In contrast, the lower spin states have larger $2\pi^*$ populations than the $^5\Delta_g$ state, so that the net backdonation per CO is very similar to the TiCO states. Thus, the Ti–C bond lengths for the lower spin states are shorter than the $^5\Delta_g$ state, and the C–O bond lengths are greater.

The bonding mechanisms of the Ti(CO)$_2$ states in Table VII, and the differences from TiCO, can be further elucidated from the $3d$, $4s$, and $4p$ populations. Comparing first the $^5\Delta_g$ state of Ti(CO)$_2$ with the $^5\Delta$ state of TiCO, there is a larger total $3d$ population for Ti(CO)$_2$ but smaller $4s$ and $4p$ populations. Thus, the second CO molecule inhibits $4s–4p_\sigma$ hybridization, but favors $4s$ to $3d$ promotion, simultaneously reducing the σ repulsion and retaining a $3d$ population of $2.9e$ even though $0.6e$ are donated to the CO in the π space. For the lower spin states, the $4s$ population is reduced markedly, which implies a large amount of $4s$ to $3d$ promotion, with subsequent back donation to the CO molecules. The very large $2\pi^*$ populations come about even though the Ti atom has lost only about $0.6–0.7e$ in overall charge, indicating that as well as $4s$ to $3d$ promotion, there is 5σ to $4s$ and $3d$ donation. Thus, there is a rearrangement of charge in the CO σ space in the lower spin states of the dicarbonyl which does

TABLE VI. Summary of the $M(CO)_2$ CASSCF/MRCI state orderings.[a]

State	Occupation	Active space[b]	ΔE_{CAS}	ΔE_{CI}
$Ti(CO)_2(4e)$				
$^5\Delta_g$	$\sigma_g^1 \delta_g^1 \pi_g^2$	41 121 220	0.00	0.00
$^3\Pi_g$	$\sigma_g^1 \pi_g^3, \delta_g^1 \pi_g^3$	42 220 330	-0.04	0.05
$^1\Sigma_g^+$	π_g^4	11 110 220	0.14	0.06
$^5\Pi_u$	$\sigma_g^1 \pi_u^1 \pi_g^2, \delta_g^1 \pi_u^1 \pi_g^2$	42 220 330	0.13	0.21
$^3\Pi_u$	$\sigma_g^1 \pi_u^1 \pi_g^2, \delta_g^1 \pi_u^1 \pi_g^2$	42 220 330	0.37	0.44
$^3\Gamma_g$ [c]	$\sigma_g^1 \delta_g^1 \pi_g^2$	41 121 220	0.54	0.41
$^1\Phi_g$ [d]	$\delta_g^1 \pi_g^3, \delta_g^1 \pi_g^1 \pi_u^2$	22 220 330	0.67	0.73
$^1\Delta_g$ [d]	$\sigma_g^2 \pi_g^2, \delta_g^2 \pi_g^2, \sigma_g^1 \delta_g^1 \pi_g^2$	41 121 220	0.99	0.79
$^1\Phi_u$ [d]	$\sigma_g^1 \pi_u^1 \pi_g^2, \delta_g^1 \pi_u^1 \pi_g^2$	42 220 330	0.91	0.96
$^5\Phi_g$ [d]	$\delta_g^1 \pi_u^2 \pi_g^1$	22 220 330	1.51	1.62
$Sc(CO)_2(3e)$				
$^4\Sigma_g^-$	$\sigma_g^1 \pi_g^2$	21 100 220	0.00	0.00
$^2\Pi_g$	π_g^3	01 100 220	-0.14	-0.09
$^2\Pi_u$	$\pi_u^1 \pi_g^2$	02 200 220	0.29	0.33
$^4\Delta_g$	$\delta_g^1 \pi_g^2, \delta_g^1 \pi_u^2$	22 220 220	0.37	0.47
$V(CO)_2(5e)$				
$^6\Sigma_g^+$	$\sigma_g^1 \delta_g^2 \pi_g^2$	40 020 220	0.00	0.00
$^4\Pi_g$	$\sigma_g^1 \delta_g^1 \pi_g^3, \delta_g^2 \pi_g^3$	41 120 220	0.25	0.25
$^4\Delta_g$	$\sigma_g^2 \delta_g^1 \pi_g^2$	41 120 220	0.47	0.43
$^2\Delta_g$ [e]	$\delta_g^1 \pi_g^4$	21 120 220	0.57	0.51
$^4\Pi_u$	$\sigma_g^1 \delta_g^1 \pi_u^1 \pi_g^2, \delta_g^2 \pi_u^1 \pi_g^2$	42 220 220	0.69	0.72
$^4\Sigma_u^+$ [f]	$\sigma_g^1 \delta_g^2 \pi_g^1 \pi_u^1$	42 220 220	0.99	1.10

[a] Energy differences are in eV. Except where indicated, the bond lengths are the optimal geometries given in Table VII.

[b] The notation refers to the number of active orbitals in the $a_g, b_{2u}, b_{3u}, b_{1g}, b_{1u}, b_{2g}, b_{3g}$, and a_u irreducible representations in D_{2h} symmetry.

[c] The $^3\Gamma_g$ state is unbound at the CASSCF level, and has only a very shallow minimum in the potential curve at the MRCI level.

[d] The geometries of these states are not optimized. The bond lengths are $r(Ti-C) = 4.202\ a_0$ and $r(C-O) = 2.144\ a_0$.

[e] The $^2\Sigma_g^+$ ($\sigma_g^1 \pi_g^4$) state lies about 0.7 eV above the $^2\Delta_g$ state at the CASSCF level of treatment, at the same bond length. The bond length for the $^2\Sigma_g^+$ CASSCF/MRCI calculation was $r(Ti-C) = 4.102\ a_0$, $r(C-O) = 2.165\ a_0$, optimized at the CASSCF(5e) level of calculation.

[f] The bond length for the $^4\Sigma_u^+$ CASSCF/MRCI calculation was $r(Ti-C) = 4.102\ a_0$, $r(C-O) = 2.165\ a_0$, optimized at the CASSCF(5e) level of calculation.

not occur to the same extent in the high-spin ground state or in the monocarbonyl. The $3d$ population is reduced in the Π_u states, but the $4p_\pi$ population is significantly increased, indicating increased $4p_\pi-2\pi^*$ interaction. The close proximity of the lower spin states to the $^5\Delta_g$ state, when compared to the separations for TiCO, illustrates the destabilization of the high-spin state and the significant stabilization of the lower spin states in the dicarbonyl.

The lowest states of $Ti(CO)_2$ are so close in energy at the $4e$ CASSCF/MRCI level of theory that it is difficult to unambiguously determine which is the true ground state, as the errors in the computed separations are too large at this level of theory. Thus, for the $^5\Delta_g$, $^3\Pi_g$, and $^1\Sigma_g^+$ states we have carried out selected reference MRCI calculations, as outlined in Sec. II, correlating the Ti $3d$ and $4s$ electrons, as well as the CO 5σ and 1π electrons. These were carried out at

fixed geometry, taken from the $4e$ CASSCF/MRCI calculations. Table VIII gives some details of these calculations.

Since we wish to accurately calculate the energy separations between the states, we must treat them on an equal footing. One measure of the quality of the MRCI wave function is the percentage of the reference space in the final wave function, denoted Ref% in Table VIII. If the separations are to be reliable, the reference percentage must be comparable for each state. However, it is difficult to treat the three states equally well. At a reference selection threshold of 0.075, the $^3\Pi_g$ state has a very large number of configurations, whereas the $^5\Delta_g$ and $^1\Sigma_g^+$ states have much fewer. Thus, we carried out the calculations on the latter two states at the 0.075 threshold, giving reference percentages of around 87%. A second selection threshold of 0.100 was used in order to reduce the number of configurations for the $^3\Pi_g$ state. How-

TABLE VII. Summary of the $M(CO)_2$ CASSCF/MRCI geometries and populations.[a]

State	r(M–C)	r(C–O)	$3d$	$4s$	$4p_\sigma$	$4p_\pi$	$2\pi^*$
$Ti(CO)_2(4e)$							
$^5\Delta_g$ (CASSCF)	4.145	2.158	2.92	0.68	0.11	0.03	0.61
$^5\Delta_g$ (MRCI)	4.145	2.158	2.91	0.69	0.11	0.04	0.65
$^3\Pi_g$ (CASSCF)	3.992	2.197	2.86	0.26	0.17	0.08	1.17
$^3\Pi_g$ (MRCI)	3.992	2.197	2.86	0.28	0.17	0.08	1.15
$^1\Sigma_g^+$ (CASSCF)	3.860	2.211	2.87	0.20	0.19	0.05	1.29
$^1\Sigma_g^+$ (MRCI)	3.870	2.210	2.87	0.20	0.20	0.06	1.28
$^5\Pi_u$ (CASSCF)	4.085	2.193	2.62	0.22	0.16	0.35	1.15
$^5\Pi_u$ (MRCI)	4.093	2.186	2.61	0.26	0.16	0.39	1.09
$^3\Pi_u$ (CASSCF)	4.073	2.190	2.58	0.25	0.16	0.36	1.16
$^3\Pi_u$ (MRCI)	4.073	2.190	2.58	0.26	0.17	0.38	1.13
$Sc(CO)_2(3e)$							
$^4\Sigma_g^-$ (CASSCF)	4.213	2.175	1.59	0.75	0.12	0.10	0.87
$^4\Sigma_g^-$ (MRCI)	4.226	2.173	1.58	0.76	0.12	0.11	0.85
$^2\Pi_g$ (CASSCF)	4.106	2.216	1.72	0.18	0.17	0.09	1.38
$^2\Pi_g$ (MRCI)	4.106	2.216	1.73	0.18	0.17	0.09	1.36
$^2\Pi_u$ (CASSCF)	4.163	2.209	1.50	0.19	0.15	0.32	1.36
$^2\Pi_u$ (MRCI)	4.163	2.209	1.51	0.19	0.17	0.34	1.33
$^4\Delta_g$ (CASSCF)	4.279	2.207	1.71	0.16	0.15	0.16	1.30
$^4\Delta_g$ (MRCI)	4.279	2.207	1.72	0.16	0.15	0.16	1.29
$V(CO)_2(5e)$							
$^6\Sigma_g^+$ (CASSCF)	4.138	2.138	4.23	0.62	0.09	0.00	0.35
$^6\Sigma_g^+$ (MRCI)	4.115	2.143	4.18	0.60	0.09	0.02	0.41
$^4\Pi_g$ (CASSCF)	3.871	2.181	3.90	0.48	0.16	0.05	0.92
$^4\Pi_g$[b](MRCI)	3.871	2.181	3.88	0.52	0.16	0.05	0.90
$^4\Delta_g$ (CASSCF)	4.239	2.122	3.69	1.16	0.08	0.18	0.15
$^4\Delta_g$[b](MRCI)	4.239	2.122	3.68	1.14	0.09	0.18	0.18
$^2\Delta_g$ (CASSCF)	3.775	2.204	3.96	0.21	0.20	0.05	1.21
$^2\Delta_g$[b](MRCI)	3.775	2.204	3.95	0.21	0.20	0.06	1.20
$^4\Pi_u$ (CASSCF)	3.991	2.175	3.61	0.44	0.15	0.42	0.94
$^4\Pi_u$[b](MRCI)	3.991	2.175	3.59	0.41	0.16	0.43	0.91

[a] Bond lengths are in a_0.
[b] The geometries for these calculations are taken from the optimized CASSCF calculations on the same state. All other geometries are optimized.

ever, the reference percentage is much lower than for the $^5\Delta_g$ and $^1\Sigma_g^+$ states, also treated at the 0.100 selection threshold, making the predicted separations unreliable. Thus, a second calculation was carried out on the $^3\Pi_g$ state at a selection threshold of 0.089, which leads to a reference percentage of 86.3%, significantly closer to either the 0.075 or 0.100 selection threshold results for the other two states. This result allows us to make much more reliable predictions regarding the separations between these states (see discussion below).

The results of the more extensive MRCI calculations on $Ti(CO)_2$ are given in Table IX. The separation and charge distributions for the $^5\Delta_g$ and $^1\Sigma_g^+$ states are very similar with either selection threshold, and adding the Davidson correction does not alter the separation appreciably. For the $^3\Pi_g$ state there is a 0.35 eV difference between the energy separations calculated at the two selection thresholds, but this is reduced to 0.01 eV when the Davidson correction is included. Coupled with the fact that the Davidson correction is much smaller for the 0.089 threshold than the 0.100 threshold calculation, this implies that the $^3\Pi_g$ results are

nearly converged, and that the prediction separation at the 0.089 threshold including the Davidson correction should be reliable. Thus we feel that the prediction of a $^5\Delta_g$ ground state for $Ti(CO)_2$ should be fairly reliable, with the $^1\Sigma_g^+$ and $^3\Pi_g$ states being almost degenerate, lying between 0.15 and 0.20 eV higher in energy.

A comparison of the $16e$ MRCI results of Table IX with the $4e$ results of Table VI and VII is quite interesting. Correlating more electrons favors the $^5\Delta_g$ state, which is counterintuitive since one usually expects the higher spin states to be better treated at a lower level of theory. The populations show that there is a differential relaxation effect when correlating the 5σ electrons on the CO ligands: there is more promotion of charge from the $4s$ to the $3d$ shell in the $16e$ treatments of the lower spin states, compared to the $4e$ treatment. This does not occur for the high-spin $^5\Delta_g$ state, possibly because of the longer M–C bond length. However, this relaxation effect would be expected to stabilize the lower spin states. Alternatively, the lower spin states may include more CO correlation at the $4e$ level, due to the greater back dona-

TABLE VIII. Details of the $M(CO)_2$ large scale MRCI calculations.

	Threshold	$N_{ref,occ}$	$N_{ref,csf}$	N_{csf}	Ref%
$Ti(CO)_2(16e)$					
$^5\Delta_g$	0.075	6	6	866 178	87.5
$^5\Delta_g$	0.100	5	5	735 198	87.3
$^1\Sigma_g^+$	0.075	11	17	799 017	87.4
$^1\Sigma_g^+$	0.100	10	15	680 596	87.4
$^3\Pi_g$	0.075	18	34	2 413 684	$\cdots$
$^3\Pi_g$	0.089	13	25	1 805 180	86.3
$^3\Pi_g$	0.100	8	14	1 063 403	83.4
$Sc(CO)_2(15e)$					
$^4\Sigma_g^-$	0.075	6	6	597 853	87.9
$^4\Sigma_g^-$	0.100	5	5	508 539	87.8
$^2\Pi_g$	0.075	8	12	568 789	88.3
$^2\Pi_g$	0.100	7	10	491 002	88.1
$^2\Pi_u$	0.075/0.100	8	13	617 115	88.1
$^4\Delta_g$	0.075/0.100	2	2	202 138	88.2
$V(CO)_2(17e)$					
$^6\Sigma_g^+$	0.075/0.100	5	5	982 269	86.9
$^4\Pi_g$	0.075	15	39	3 746 353	$\cdots$
$^4\Pi_g$	0.085	12	27	2 721 736	85.3
$^4\Pi_g$	0.090	9	15	1 636 269	84.3
$^4\Pi_g$	0.100	7	10	1 138 089	84.1
$^4\Delta_g$	0.075	8	17	1 729 181	87.1
$^4\Delta_g$	0.100	7	16	1 604 315	87.1

TABLE IX. Summary of the $M(CO)_2$ large scale MRCI results.[a]

	$r(M-C)$	$r(C-O)$	ΔE [b]	$3d$	$4s$	$4p_\sigma$	$4p_\pi$	$2\pi^*$
$Ti(CO)_2(16e)$								
$^5\Delta_g$ MRCI(0.075)	4.145	2.158	0.00(0.00)	2.92	0.68	0.11	0.03	0.62
$^5\Delta_g$ MRCI(0.100)	4.145	2.158	0.00(0.00)	2.96	0.69	0.12	0.01	0.61
$^1\Sigma_g^+$ MRCI(0.075)	3.870	2.210	0.18(0.16)	2.95	0.21	0.21	0.06	1.22
$^1\Sigma_g^+$ MRCI(0.100)	3.870	2.210	0.17(0.16)	2.95	0.21	0.21	0.06	1.22
$^3\Pi_g$ MRCI(0.089)	3.992	2.197	0.30(0.19)	2.95	0.21	0.18	0.08	1.16
$^3\Pi_g$ MRCI(0.100)	3.992	2.197	0.65(0.20)	3.00	0.22	0.18	0.05	1.12
$Sc(CO)_2(15e)$								
$^4\Sigma_g^-$ MRCI(0.075)	4.226	2.173	0.00(0.00)	1.62	0.76	0.13	0.11	0.84
$^4\Sigma_g^-$ MRCI(0.100)	4.226	2.173	0.00(0.00)	1.63	0.77	0.13	0.10	0.83
$^2\Pi_g$ MRCI(0.075)	4.106	2.216	0.00(0.03)	1.80	0.19	0.18	0.09	1.31
$^2\Pi_g$ MRCI(0.100)	4.106	2.216	0.01(0.04)	1.82	0.19	0.18	0.09	1.29
$^2\Pi_u$ MRCI(0.075)	4.163	2.209	0.42(0.44)	1.56	0.20	0.18	0.36	1.29
$^2\Pi_u$ MRCI(0.100)			0.39(0.43)					
$^4\Delta_g$ MRCI(0.075)	4.279	2.207	0.65(0.68)	1.75	0.18	0.16	0.18	1.25
$^4\Delta_g$ MRCI(0.100)			0.62(0.67)					
$V(CO)_2(17e)$								
$^6\Sigma_g^+$ MRCI(0.075/0.100)	4.115	2.143	0.00(0.00)	4.19	0.64	0.10	0.01	0.40
$^4\Pi_g$ MRCI(0.085)	3.871	2.181	0.36(0.15)	3.90	0.59	0.17	0.03	0.87
$^4\Pi_g$ MRCI(0.090)	3.871	2.181	0.52(0.17)	3.92	0.56	0.17	0.04	0.87
$^4\Pi_g$ MRCI(0.100)	3.871	2.181	0.82(0.43)	3.97	0.58	0.17	0.02	0.81
$^4\Delta_g$ MRCI(0.075)	4.239	2.122	0.48(0.52)	3.69	1.20	0.09	0.16	0.17
$^4\Delta_g$ MRCI(0.100)	4.239	2.122	0.49(0.53)	3.69	1.21	0.09	0.16	0.17

[a] Bond lengths are in a_0, and dissociation energies in eV. The bond lengths are taken from Table VIII.
[b] The values in parentheses include the Davidson correction ($+ Q$).

tion to the CO ligands. The 16e MRCI calculations then present a more balanced picture of the CO correlation between the low- and high-spin states. However, the separations and charge distributions from the 4e calculations are very satifactory for such relatively simple calculations.

We now consider D_e [Ti–(CO)$_2$], for the $^5\Delta_g$ ground state. We again use the MCPF method, investigating the effect of correlating more electrons as in the monocarbonyls, and comparing with the MRCI results. In this case, the 16e MRCI results provide an additional calibration of the MCPF method. The results are presented in Table X.

The 4e MCPF D_e is lower than either the CASSCF or the MRCI 4e results, so the agreement between the MCPF and MRCI results is not as good as found for TiCO: the 4e MCPF treatment underestimates the 3d_π back donation to the CO molecules by $\approx 28\%$ compared with the CASSCF/ MRCI treatment, and this leads to the smaller binding energy for the MCPF wave function.

The dependence of D_e, the charge distribution, and bond lengths on the number of electrons correlated is qualitatively similar to that found for TiCO. The most important

contribution to D_e results from correlating the CO valence electrons where the binding energy increases by 0.76 eV, or 0.38 eV per CO. This is to be compared with 0.47 eV found for TiCO. Thus, the binding energy of the second CO is smaller than the first. The 3$s3p$ correlation, in the 32e treatment, has a contribution to D_e of slightly larger magnitude than found for TiCO. Thus, for both TiCO and Ti(CO)$_2$ it is necessary to correlate all the valence electrons *and* the Ti 3s and 3p electrons to determine D_e accurately. There is an increase in the π back donation upon going from the 4e to the 24e treatment, and consequently an increase in the C–O bond length. The Ti–C bond length decreases with increasing D_e, and there is a small rearrangement of charge on the Ti, mainly in the 4p_σ population.

The 16e MRCI and MCPF treatments provide additional information. The 16e MCPF D_e differs from the 16e MRCI + Q D_e by about the same percentage as the 4e MCPF and MRCI results, relative to the 3d ^{3}4s^1 asymptote. (We note that for the 4e treatment the Davidson correction is very small. Also, the 0.100 threshold 16e MRCI wave function gives D_e values very close to the 0.075 threshold

TABLE X. Comparison of the CASSCF/MRCI and MCPF results for the M(CO)$_2$ molecules.[a]

	r(M–C)	r(C–O)	D_e[b]	3d	4s	4p_σ	4p_π	2π^*
Ti(CO)$_2$($^5\Delta_g$)								
CAS(4e)	4.145	2.158	0.74(− 0.04)	2.92	0.68	0.11	0.03	0.61
MRCI(4e)	4.145	2.158	0.81(0.03)	2.91	0.69	0.11	0.04	0.65
MRCI(16e,0.075)[c]	4.145	2.158	1.36(0.58)	2.92	0.68	0.11	0.03	0.62
MRCI(16e + Q,0.075)[c]	4.145	2.158	1.49(0.71)					
MCPF(4e)	4.169	2.150	0.68(− 0.10)	3.01	0.71	0.08	0.01	0.47
MCPF(16e)[c]	4.145	2.158	1.29(0.51)	2.99	0.75	0.13	0.02	0.56
MCPF(16e)	4.110	2.203	1.26(0.48)	2.97	0.74	0.12	0.02	0.60
MCPF(24e)	4.098	2.221	1.44(0.66)	2.96	0.76	0.15	0.02	0.65
MCPF(32e)	4.080	2.221	1.59(0.81)	2.99	0.76	0.11	0.00	0.69
Sc(CO)$_2$($^4\Sigma_g^-$)								
CAS(3e)	4.213	2.175	1.05(− 0.38)	1.59	0.75	0.12	0.10	0.87
MRCI(3e)	4.226	2.173	1.14(− 0.29)	1.58	0.76	0.12	0.11	0.85
MRCI(15e,0.075)[c]	4.226	2.173	1.70(0.27)	1.62	0.76	0.13	0.11	0.84
MRCI(15e + Q,0.075)[c]	4.226	2.173	1.80(0.37)					
MCPF(3e)	4.240	2.164	0.95(− 0.48)	1.76	0.79	0.09	0.04	0.65
MCPF(15e)[c]	4.226	2.173	1.54(0.11)	1.77	0.83	0.13	0.04	0.69
MCPF(23e)	4.160	2.246	1.68(0.25)	1.72	0.84	0.16	0.05	0.81
MCPF(31e)	4.168	2.239	1.90(0.47)	1.77	0.84	0.11	0.00	0.83
V(CO)$_2$($^6\Sigma_g^+$)								
CAS(5e)	4.138	2.138	0.39(0.15)	4.23	0.62	0.09	0.00	0.35
MRCI(5e)	4.115	2.143	0.62(0.38)	4.18	0.60	0.09	0.02	0.41
MRCI(17e,0.075/0.100)[c]	4.115	2.143	1.04(0.80)	4.19	0.64	0.10	0.01	0.40
MRCI(17e + Q,0.075/ 0.100)[c]	4.115	2.143	1.23(0.99)					
MCPF(5e)	4.117	2.139	0.50(0.26)	4.19	0.63	0.07	0.01	0.35
MCPF(17e)[c]	4.145	2.143	1.10(0.86)	4.17	0.68	0.12	0.01	0.44
MCPF(25e)	4.019	2.213	1.28(1.04)	4.14	0.68	0.15	0.02	0.55
MCPF(33e)[c]	4.019	2.213	1.39(1.15)	4.16	0.69	0.11	0.00	0.58

[a] Bond lengths are in a_0, and dissociation energies in eV.
[b] Relative to Ti$^5F(3d^34s^1)$, Sc$^4F(3d^24s^1)$, V$^6D(3d^44s^1)$, respectively, and two CO$^1\Sigma^+$ molecules. The values in parentheses are relative to Ti$^3F(3d^24s^2)$, Sc$^2D(3d^14s^2)$, V$^4F(3d^34s^2)$, respectively, and CO$^1\Sigma^+$, corrected using the experimental 3$d^{n+1}4s^1$ − 3d^n4s^2 separation. The CASSCF/MRCI D_e values are computed relative to an M–(CO)$_2$ supermolecule [r(M–C) = 100.0 a_0, r(C–O) = 2.12 a_0], in order to reduce size consistency errors.
[c] The bond lengths are not optimized.

case.) Thus, the $16e$ MCPF calculations seem to have about the same relative accuracy in D_e as the $4e$ calculations. We note that the $16e$ MRCI D_e values are calculated relative to a supermolecule with the CO fragment having the SCF bond length. This reduces the error in D_e due from using the equilibrium geometry of the $4e$ calculations for the $16e$ MRCI calculations. The two $16e$ MCPF calculations of Table X illustrate this point: the first is at the $4e$ CASSCF/MRCI geometry, whereas the second has been fully optimized. Also, the first has D_e calculated relative to a CO at the SCF bond length, whereas the second has D_e calculated relative to CO at the $6e$ MCPF bond length, as given in Table II. The two D_e values are very close, illustrating the consistency of this approach.

Comparing the MCPF and MRCI results for Ti(CO)$_2$, and taking into account the basis set superposition error as in TiCO, our best estimate for D_e [Ti–(CO)$_2$] is 1.80 eV relative to the $3d\,^3 4s^1\,(^5F)$ atomic asymptote. The binding energy per carbonyl in Ti(CO)$_2$ is only 63% of the TiCO value, mainly because the high-spin states are less favorable for the dicarbonyl compared to the monocarbonyl complexes, as discussed previously.

E. Sc(CO)₂

The treatment of Sc(CO)$_2$ is similar to that of Ti(CO)$_2$. The ordering of the low-lying quartet and doublet states of Sc(CO)$_2$ are given in Table VI. As for Ti(CO)$_2$, configurations with more π electrons are much more important than in the monocarbonyl, and at this level of treatment there is a low-spin $^2\Pi_g$ ground state. The $^4\Sigma_g^-$ state, which is directly related to the $^4\Sigma^-$ ground state of ScCO, lies very close to the ground state. The $^2\Pi_u$ and $^4\Delta_g$ state lie some 0.4 eV above the ground state.

The geometries and populations for Sc(CO)$_2$ presented in Table VII follow similar trends to those of Ti(CO)$_2$. In general, however, the π backdonation is significantly larger in Sc(CO)$_2$. For example, there is $0.2e$ more back donation in the $^4\Sigma_g^-$ state of Sc(CO)$_2$ than in the $^5\Delta_g$ state of Ti(CO)$_2$. This is similar to the effect in the monocarbonyls, although in general somewhat larger in the dicarbonyls. The M–C bond lengths are greater than the analogous states in Ti(CO)$_2$, despite the higher back donation. This may be due to the more diffuse nature of the orbitals in Sc than Ti, as noted previously.

The variation in populations and bond lengths among the different states of Sc(CO)$_2$ is similar to that found for the analogous states of Ti(CO)$_2$. The $4s$ population is very low in the low-spin states, with $4s$ to $3d$ promotion and subsequent backdonation being the important bonding mechanism, with an underlying 5σ donation to the metal. The $0.69e$ backdonation per CO molecule for the $^2\Pi_g$ state is very large, surpassing the donation in the $^4\Sigma^-$ ground state of ScCO. The $^4\Delta_g$ state has a large Sc–C bond length, even with a large back donation. The dominant configurations, given in Table VI, indicate an important contribution from the π_u orbitals for this state, which probably accounts for the large Sc–C bond length. The low $4s$ population of the $^4\Delta_g$ state arises because this state is nominally $3d^3$, with the $4s$ population coming from 5σ to $4s$ donation.

To define more accurately the separations between the low-lying states of Sc(CO)$_2$, we have carried out more extensive MRCI calculations, analogous to the $16e$ calculations for Ti(CO)$_2$. These are more straightforward calculations, however, due to the smaller number of configurations, as may be seen in Table VIII. The reference percentage is nearly constant at 88% with either selection threshold, so that the predicted separations should be reliable. The results of these calculations are given in Table IX. The $^4\Sigma_g^-$ state is favored by correlating more electrons, becoming essentially degenerate with the $^2\Pi_g$ state, with the $^2\Pi_u$ and $^4\Delta_g$ states lying relatively high in energy. A similar trend between the high- and low-spin states was noted for Ti(CO)$_2$. Comparing the $15e$ MRCI populations with the $3e$ results of Table VII, there is generally good agreement, with only small rearrangements in charge. Overall, the $3e$ results are very satisfactory.

We now consider D_e as a function of the number of electrons correlated for the $^4\Sigma_g^-$ state, using the MCPF method. The results are given in Table X, along with the $3e$ CASSCF/MRCI and $15e$ MRCI results for comparison. The $3e$ MCPF results are similar to the $4e$ results for Ti(CO)$_2$: the $3e$ MCPF D_e for Sc(CO)$_2$ is significantly smaller than the $3e$ MRCI D_e, so that the agreement is again not as good as for the monocarbonyl, because the $3d_\pi$ backdonation is underestimated in the MCPF calculation. However, the MCPF results are still expected to reliably indicate the effect on D_e of correlating more electrons.

At the $15e$ level, the MCPF D_e value is lower than the MRCI $+ Q$ value by about the same percentage as the $3e$ calculations, indicating that as for Ti(CO)$_2$ the errors seem to be roughly proportional to the number of electrons correlated. As for the $3e$ calculations, the backdonation is underestimated at the MCPF level. As we correlate more electrons, D_e is again increased with a 0.22 eV effect from $3s3p$ correlation, to be compared with only 0.13 eV for ScCO. The $3s3p$ correlation is expected to be more important in the dicarbonyls due to the additional repulsion from the second 5σ lone pair.

Our best estimate of D_e [Sc–(CO)$_2$] is 2.20 eV relative to the $3d\,^2 4s^1\,(^4F)$ atomic asymptote. The binding energy per carbonyl in Sc(CO)$_2$ is only 64% of the ScCO value, a result similar to that found for TiCO and Ti(CO)$_2$.

F. V(CO)₂

The final system to be discussed is V(CO)$_2$. The results of the $5e$ CASSCF/MRCI calculations are given in Tables VI and VII. At this level of treatment, V(CO)$_2$ has a $^6\Sigma_g^+$ ground state, with a low-lying $^4\Pi_g$ state. The $^6\Sigma_g^+$ state is directly related to the $^6\Sigma^+$ state of VCO, whereas the other low-lying states do not have any configurational analogue in VCO. As for Ti(CO)$_2$ and Sc(CO)$_2$, the important configurations in the low-lying states have more π electrons than in the monocarbonyl. The backdonation for the $^6\Sigma_g^+$ state of V(CO)$_2$ is less than in either the $^5\Delta_g$ state of Ti(CO)$_2$ or the $^4\Sigma_g^-$ state of Sc(CO)$_2$, the small $0.2e$ backdonation per CO leading to a short C–O bond distance. The $^4\Pi_g$ state of

$V(CO)_2$ is related to the $^3\Pi_g$ and $^2\Pi_g$ states of $Ti(CO)_2$ and $Sc(CO)_2$ simply in the number of (nonbonding) $3d_\delta$-type electrons, just as the high-spin states of the three molecules are related. The bond lengths and populations illustrate this relationship, with large backdonation and reduced $3d$ and $4s$ populations in all three states. The backdonation in the $^4\Pi_g$ state of $V(CO)_2$ is lower than the analogous states in $Ti(CO)_2$ and $Sc(CO)_2$, and the $4s$ population is higher, a trend consistently seen among the three transition metal atoms. We note that the $^4\Pi_u$, $^3\Pi_u$, and $^2\Pi_u$ states of $V(CO)_2$, $Ti(CO)_2$, and $Sc(CO)_2$ are similarly related.

The $^4\Delta_g$ state of $V(CO)_2$ is unique among the monocarbonyl and dicarbonyl bound states because of the large $4s$ population, and very small $0.18e$ backdonation in the MRCI treatment. This state has a σ_g orbital which is doubly occupied in the dominant configuration, and which is a metal centered $4s$–$3d_\sigma$ orbital. This occupation necessitates a large V–C bond distance and so reduces the effectiveness of $3d_\pi$ to $2\pi^*$ backdonation, leading to the short C–O bond distance.

We have carried out large-scale MRCI calculations on the lowest three states of $V(CO)_2$ in order to more quantitatively determine the separations. The details of these calculations are given in Table VIII. As for $Ti(CO)_2$ and $Sc(CO)_2$, we have used different reference selection thresholds in order to make the calculations tractable. The $^4\Pi_g$ state has a very large number of configurations at a selection threshold of 0.075, whereas the $^6\Sigma_g^+$ and $^4\Delta_g$ states have much fewer configurations. The reference percentages of Table VIII indicate that the $^6\Sigma_g^+$ and $^4\Delta_g$ states will be described with a similar accuracy at either the 0.075 or 0.100 selection threshold, whereas the $^4\Pi_g$ state has a lower reference percentage at the 0.100 threshold. The selection threshold of 0.085 leads to a significantly better reference percentage for the $^4\Pi_g$ state, albeit at a large increase in computational cost.

In Table IX we present the energy separations and the Mulliken populations from the large scale MRCI calculations on $V(CO)_2$. For the $^4\Delta_g$ state, changing the selection threshold only changes the separation and populations by a small amount, and the Davidson correction is quite small. For the $^4\Pi_g$ state reducing the threshold from 0.100 to 0.090 leads to a large change in the $^4\Pi_g$–$^6\Sigma_g^+$ separation, with or without the Davidson correction. However, between the 0.090 and 0.085 threshold calculations there is a significantly smaller change at the MRCI level, and a very small 0.02 eV change with the Davidson correction. In addition, the Davidson correction is much smaller with the 0.085 selection threshold than the 0.090 threshold. Thus, we would predict the $^4\Pi_g$ state to lie between 0.1 and 0.15 eV above the $^6\Sigma_g^+$ state. We also note that the $5e$ CASSCF/MRCI treatment gave reliable results for the separations and charge distributions in these states, as found for the $Ti(CO)_2$ $4e$ and $Sc(CO)_2$ $3e$ CASSCF/MRCI treatments.

In Table X we consider the D_e value of the $^6\Sigma_g^+$ state, and the effect of correlating more electrons. The results are similar to the other cases already considered: as we correlate more electrons, the D_e increases with backdonation increasing and the bond lengths changing accordingly. The agreement between the $5e$ MCPF and $5e$ CASSCF/MRCI results is similar to $Ti(CO)_2$, and somewhat better than VCO. At

the $17e$ level the agreement is again reasonable, with the error less than at the $5e$ level.

Our best estimate for D_e [V–$(CO)_2$] is 1.60 eV, relative to the $3d^44s^1$ (^6D) atomic asymptote. Thus, as for the monocarbonyl complexes, V forms the most weakly bound dicarbonyl complex. The dissociation energy per carbonyl for $V(CO)_2$ is 70% that of VCO, which is similar to the result found for the Ti and Sc complexes. Thus in all three cases, the high-spin state is less favored in the dicarbonyl than in the monocarbonyl complexes.

G. Comparison with experimental data

As noted previously, the metal atoms in the ground state MCO and $M(CO)_2$ molecules considered in this work have populations that are consistent with the $3d^{n+1}4s^1$ occupation of the metal, and so we have computed our D_e values relative to this asymptote. This corresponds to a diabatic dissociation and may be the observed D_e in some experiments. However, many experiments measure D_e relative to the ground state metal atom and we convert our computed value to this asymptote using the experimental atomic separation. This procedure avoids introducing additional errors into the D_e values from errors in the computed atomic $3d^n4s^2$–$3d^{n+1}4s^1$ separation. Our best estimate for the D_e values are given in Table XI, including an estimated error value.

In the recent experiment of Gole et al.,[6] $Ti(CO)_x$ was formed on a hot filament and reacted with O_3 to form TiO^*. The difference in the threshold for TiO emission between bare Ti and the $Ti(CO)_x$ species then yields an estimate for the Ti–$(CO)_x$ binding energy. The relation to the true binding energy depends on the density of states in TiO, and whether the $Ti(CO)_x$, O_2, and CO species are formed in their ground electronic and vibrational states. Gole et al. predict a Ti–$(CO)_x$ binding energy of ≈ 1.75 eV. If the measured D_e corresponded to the diabatic value, theory and experiment would be in reasonable agreement (see Table XI). However, this would imply that O_3 is reacting selectively with excited Ti $3d^34s^1$ atoms, which is unlikely. Alternative-

TABLE XI. Best estimate of D_e values and estimated errors for the MCO and $M(CO)_2$ molecules.

	D_e[a]	Error
ScCO	1.70(0.27)	0.15
TiCO	1.40(0.62)	0.20
VCO	1.15(0.90)	0.30
$Sc(CO)_2$	2.20(0.77)	0.45
$Ti(CO)_2$	1.80(1.02)	0.35
$V(CO)_2$	1.60(1.35)	0.35

[a] Dissociation energies and estimated errors are in eV. Dissociation energies are relative to $Sc^4F(3d^24s^1)$, $Ti^5F(3d^34s^1)$, $V^6D(3d^44s^1)$, respectively, and two $CO^1\Sigma^+$ molecules. The values in parentheses are relative to $Sc^2D(3d^14s^2)$, $Ti^3F(3d^24s^2)$, $V^4F(3d^34s^2)$, respectively, and $CO^1\Sigma^+$, corrected using the experimental $3d^{n+1}4s^1$ – $3d^n4s^2$ separation.
[b] Errors are based on the extrapolation procedure described in the text and an estimate of basis set superposition error.

ly, for the discrepancy between theory and experiment to be due to vibrational effects, the CO would have to be preferentially formed in at least the $v = 1$ vibrational level. This is heavily dependent on the form of the potential energy surface for the reaction. We note that in the photodissociation of $Fe(CO)_5$, the vibrational distribution of the ejected CO molecules is predominantly $v = 1$.[29] However, whether this is also the case for the $Ti(CO)_x$ species is unclear. Another possibility is that theory and experiment disagree because $Ti(CO)_2$, $Ti(CO)_3$, or $Ti(CO)_4$ are being formed, as we discuss further below.

Our best estimate for D_e [$Ti–(CO)_2$] is 1.02 eV, compared to 0.62 eV for D_e ($Ti–CO$), relative to the $3d^2 4s^2 (^3F)$ atomic asymptote. If $Ti(CO)_3$ was formed rather than $TiCO$ or $Ti(CO)_2$, we estimate the D_e value to be 1.6 eV, which is in reasonable agreement with the experimental value. Our reasoning is as follows: we expect the $Ti(CO)_3$ molecule to be low spin, since the near degeneracy of the high- and low-spin states for $Ti(CO)_2$ clearly shows that the second CO can almost recover the spin recoupling energy. Thus, the third CO will probably be more strongly bound than the second, leading to our estimated D_e value of 1.6 eV. Thus, while we cannot definitively say how many CO moieties are in the $Ti(CO)_x$ species observed experimentally, it is probable that there are at least two. The experimental observation of $Ti(CO)_x$, $x \geqslant 2$, rather than $TiCO$, may be due to the greater volatility of molecules with a larger number of CO moieties: the molecules with a larger number of CO moieties are probably those most likely to leave the filament surface.[30]

As noted previously, there is some matrix ESR data for $V(CO)_x$, $x = 1,3$,[9] and some matrix IR data for $V(CO)_x$, $x = 1,5$,[8] and $ScCO$.[2] The ESR experiments were interpreted in terms of a sextet ground state for VCO and a quartet ground state for $V(CO)_2$. The ESR experiment yielded two forms of VCO, one presumed linear and the other bent, whereas the IR experiment yielded only one form of VCO, which was postulated to be bent on the basis of extended Huckel calculations and the presumption of a low-spin ground state. In contrast, the ESR experiment yielded only one form of $V(CO)_2$, with no evidence of nonlinearity, whereas the IR experiment yielded three forms of $V(CO)_2$, one linear and two bent. Finally, the CO frequency shift for $ScCO$ was found to be around 190 cm^{-1},[2] assigned to a broad peak in the IR spectrum, and the frequency shift for VCO was found to be around 240 cm^{-1}.[8] The current calculations are consistent with some, although not all, of these results.

Our prediction of a $^6\Sigma^+$ ground state for VCO is consistent with the ESR result,[9] although our prediction of a $^6\Sigma_g^+$ ground state for $V(CO)_2$ is not. The low-lying $^4\Pi_g$ state of $V(CO)_2$ would not be observed in the ESR experiment, unless the orbital degeneracy was lifted by bending. Thus, we have carried out additional CASSCF($5e$) calculations changing the geometry of the $^4\Pi_g$ state, varying the $\angle CVC$, the $\angle VCO$, and the V–C bond distance, but retaining C_{2v} symmetry. Both the $^4A_2$ and $^4B_2$ states derived from the $^4\Pi_g$ state are destabilized by bending, with the $^4A_2$ state lying lowest in energy. For small distortions, however, the bend-

ing potential is very flat: to reduce the $\angle CVC$ to 160° required less than 0.05 eV, whereas to reduce it further to 140° required an additional 0.20 eV, for the $^4A_2$ state. Thus, it seems possible that matrix effects may produce small bends which could lift the degeneracy of the $^4\Pi_g$ state of $V(CO)_2$, and allow observation of this in the ESR experiment. There is also the possibility of a bend to a C_{2h} structure, which we have not considered in the current work. Alternatively, it is conceivable that the assignment of the ESR spectrum of the dicarbonyl as a sextet state would be consistent with the experimental observations.

We have also carried out calculations changing the geometry of the $^6\Sigma_g^+$ state of $V(CO)_2$, varying only the $\angle CVC$ and retaining C_{2v} symmetry. At the CASSCF($5e$) level of treatment, the minimum energy was found at an angle of 140°, whereas at the MCPF($25e$) level the minimum was found at an angle of 150°. However, the bending potential for this state is extremely flat, the energy stabilization being only 0.02 eV at the CASSCF($5e$) level and 0.04 eV at the MCPF($25e$) level. This very flat bending potential may explain the observation of three forms of $V(CO)_2$ in the IR experiments[8]: Different matrices and preparation procedures lead to three forms of $V(CO)_2$ which are very close in energy. Overall, it seems that the current prediction of a $^6\Sigma_g^+$ ground state for $V(CO)_2$ is the most consistent with the available experimental data.

As noted above, the ESR experiments[9] indicated the presence of two forms of VCO, one linear and one bent, both being sextet states. Different unpaired s populations were deduced for the two forms: one form had 33% s character in the unpaired σ orbital, whereas the other form had only 21% s character. To investigate this point, we have carried out additional CASSCF($5e$) calculations, varying the $\angle VCO$ and the V–C bond lengths. As discussed previously, the $^6\Delta$ state of VCO was found to be 0.26 eV above the $^6\Sigma^+$ ground state for the linear geometry. Neither of these states were found to be nonlinear: e.g., to reduce the $\angle VCO$ to 165° requires 0.07 eV for the $^6\Sigma^+$ derived state, and 0.02 eV for the $^6\Delta$ derived state. To further reduce the angle to 135° requires 0.30 eV of energy for the $^6\Sigma^+$ state, and 0.15 eV for the $^6\Delta$ state. Thus, matrix effects could possibly induce small bends in VCO. We note that the discussion of the ESR results by Weltner et al.[8] implies that the bent form of the molecule would be found in the gas phase. The current calculations indicate, however, that the linear form of VCO would be found in the gas phase, and that matrix effects may be responsible for the different forms observed experimentally.

Our calculations on VCO give unpaired $4s$ populations of around 80% for both states, which is not consistent with the ESR derived results. We note that the $^6\Sigma^+$ and the $^6\Delta$ derived states become close in energy as the molecule is bent, so that at 135° the separation is less than 0.1 eV. Thus with a large bend, the character of the ground state will change considerably. Our calculations indicate that the two states become more mixed with larger bends, and the $3d$ populations change significantly, although the $4s$ population remains fairly constant.

We now consider the CO frequency shifts found for the monocarbonyls. We have carried out a simple harmonic

force field analysis of the fitted potential functions used to determine the equilibrium geometries of the monocarbonyl molecules, so as to obtain qualitative frequency shifts for the C–O stretches. Our predicted C–O frequency shifts are 330, 280 and 240 cm^{-1} for ScCO, TiCO and VCO, respectively. These frequency shifts correlate fairly well with the binding energies of Table XI, taken relative to the $3d^{n+1}4s^1$ atomic asymptote: as the binding energy decreases, the frequency shift becomes smaller. They also correlate with the π backdonation discussed earlier: as the backdonation decreases, so does the frequency shift. We note that these frequency shifts are only qualitative in nature, but should predict the relative ordering correctly. Thus, the ScCO frequency shift is expected to be larger than the TiCO shift, which in turn is expected to be larger than the VCO shift. This ordering is inconsistent with the experimental results, which give a larger frequency shift for VCO than ScCO.

H. Comparison with NiCO

It is well established that the ground state of NiCO is $^1\Sigma^+$, with a $^3\Delta$ state lying about 0.8 eV higher in energy.[3] That is, unlike ScCO, TiCO, or VCO, the low-spin monocarbonyl is the ground state. This difference arises because the $^1D(3d^94s^1)$ and $^1S(3d^{10})$ states are much lower lying in Ni than are the analogous states in Sc, Ti, or V. Thus, the lower spin states of NiCO can s–d hybridize and mix in the $3d^{n+2}$ asymptote. This also results in Ni(CO)$_x$ having a nearly equal binding energy for each CO,[31] since no changes need to occur in the Ni atomic configuration as additional CO ligands are added. This is quite different from ScCO, TiCO, and VCO, where the atomic configuration must change from high-spin coupled with $4s$–$4p_\sigma$ hybridization to reduce the repulsion for the mono- and dicarbonyl molecules, to low-spin coupled as more CO molecules are added, with repulsion reduced via $4s$–$3d_\sigma$ hybridization and mixing in of the $3d^{n+2}$ atomic asymptote.

In the dicarbonyl complexes, the extra repulsion of the second CO strongly favors the low-spin states. Based on our results it seems likely that the ground state of Ti(CO)$_3$ will be a singlet, a doublet for Sc(CO)$_3$ and either a quartet or a doublet for V(CO)$_3$. We note that ESR experiments indicate a doublet ground state for V(CO)$_3$.[9] As noted previously for Ti(CO)$_3$, we expect that the third CO in Sc(CO)$_3$ and V(CO)$_3$ will be bound more strongly than the second, and that subsequent CO moieties will be added with a similar energy to the first. It is possible that the atoms on the left-hand side of the row may not have enough $3d$ electrons to strongly bind to several carbonyls. However, we have seen evidence in the current dicarbonyl calculations that donation from the CO σ space to the metal atom, with subsequent backdonation in the π space, allows the metal atoms to strongly bind even with relatively few $3d$ electrons. Thus, while the binding of the first and second CO molecules in the Sc, Ti, and V systems is quite different to the Ni systems, it is possible that subsequent CO molecules bind in a similar manner.

IV. CONCLUSIONS

Ab initio calculations on the transition metal–carbonyl systems MCO and M(CO)$_2$, M = Ti, Sc, and V, have been presented, using large Gaussian basis sets and an extensive treatment of electron correlation. The monocarbonyl complexes favor high-spin ground states in all cases: TiCO has a $^5\Delta(\sigma^1\delta^1\pi^2)$ ground state, ScCO has a $^4\Sigma^-(\sigma^1\pi^2)$ ground state, and VCO a $^6\Sigma^+(\sigma^1\delta^2\pi^2)$ ground state. For the dicarbonyl complexes there is a competition between high-, intermediate-, and low-spin states, which are found to be very close in energy. The most accurate calculations predict a $^5\Delta_g$ ground state for Ti(CO)$_2$, a $^4\Sigma_g^-$ ground state for Sc(CO)$_2$, and a $^6\Sigma_g^+$ ground state for V(CO)$_2$. These states all have the same atomic configurations as the corresponding monocarbonyl ground states. However, for Ti(CO)$_2$ there is a $^1\Sigma_g^+$ state and a $^3\Pi_g$ state lying within about 0.15 eV of the ground state, for Sc(CO)$_2$ there is $^2\Pi_g$ state which is virtually degenerate with the ground state, and for V(CO)$_2$ there is a $^4\Pi_g$ state which lies within about 0.15 eV of the ground state. These low- and intermediate-spin states are characterized by different bonding mechanisms and bond lengths to the high-spin states.

The computed D_e (Ti–CO) is 0.62 eV, whereas D_e [Ti–(CO)$_2$] is 1.02 eV, relative to the ground state Ti atomic asymptote and CO($^1\Sigma^+$). This suggests that the recent experimental value of ≈ 1.75 eV for the binding energy of Ti(CO)$_x$ should be interpreted as giving a binding energy for Ti(CO)$_x$, $x \geqslant 2$. For all three metal atoms the binding energy per carbonyl is found to be significantly lower for the dicarbonyl complexes than the monocarbonyl complexes. This is because, for the metal atoms studied here, the high-spin states are energetically less favorable for the dicarbonyl complexes than for the monocarbonyl complexes. The lower spin dicarbonyl states cannot overcome the atomic promotion energy and spin–recoupling energy, so they are energetically slightly less favorable than the high-spin states. In contrast, in the Ni(CO)$_x$ complexes each CO binds with approximately the same energy, largely because the low-spin atomic states are readily available for binding, so that the atomic configuration does not need to change as more CO moieties are added.

For both the monocarbonyl and dicarbonyl complexes, Sc is found to be the most strongly bound, Ti the next most strongly bound, and V the most weakly bound, relative to the $3d^{n+1}4s^1$ atomic asymptote. This is interpreted in terms of the increasing ionization potential of the metal atoms and the increase in the relative size of the $4s$ orbital compared to the $3d$ orbital across the first transition row. The binding energies imply that the C–O frequency shift should be largest for ScCO, intermediate for TiCO, and smallest for VCO, and the computed frequency shifts support this prediction.

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