

Thermal stability of Group 6 bis(cyclopentadienyl) and ethylene bridged bis(cyclopentadienyl) monocarbonyl complexes; a theoretical study

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Density functional calculations have been used to estimate the energy change involved in dissociation of CO from $[M(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$ ($M = \text{Cr}, \text{Mo}$ or W) and $[\text{Cr}\{\text{C}_2\text{H}_4(\eta\text{-C}_5\text{H}_4)_2\}(\text{CO})]$ to give, in each case, free CO and a triplet metallocene product. The dissociation energy for $[\text{M}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$ is calculated to be 99 (Cr), 186 (Mo) and 194 kJ mol^{-1} (W) showing $[\text{Cr}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$ to be significantly less thermally stable than the Mo or W analogues consistent with the experimental findings. For the *ansa*-bridged compound $[\text{Cr}\{\text{C}_2\text{H}_4(\eta\text{-C}_5\text{H}_4)_2\}(\text{CO})]$ the calculated dissociation energy was 112 kJ mol^{-1} , significantly more endothermic than for $[\text{Cr}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})]$, consistent with the enhanced thermal stability found for $[\text{Cr}\{\text{C}_2\text{Me}_4(\eta\text{-C}_5\text{H}_4)_2\}(\text{CO})]$ as a result of introduction of an *ansa*-bridge. Theoretical analysis shows that the cause of the differences in thermal stability lies in the stability of the triplet metallocene product. The high spin-pairing energy for Cr favours formation of a triplet state more than is the case for Mo and W. Formation of a triplet state is of less advantage in the *ansa*-bridged free chromocene as the rings are unable to relax to a near parallel structure, thereby lowering the energy of the d electrons. Such relaxation is prevented by the presence of an *ansa*-bridge.

Introduction

The chemistry of the Group 6 metallocenes MCp_2 ($M = \text{Cr}, \text{Mo}$ or W ; $\text{Cp} = \eta\text{-C}_5\text{H}_5$) shows strong gradations in reactivity. Both MoCp_2 and WCp_2 have been characterised as matrix isolated species.¹ They are formed as reactive intermediates in a variety of reactions² and are able to form adducts *via* addition or insertion steps. Indeed, tungstenocene is capable of activating aromatic C–H bonds.^{3,4} Conversely, CrCp_2 is an easily accessible, commercially available species which does not exhibit the high reactivity of the lower Group 6 metallocenes.

Wong and Brintzinger⁵ investigated the reactivity patterns of the Group 6 metallocenes with CO as a probe of the reactivity of the free metallocene. The compounds $[\text{MoCp}_2(\text{CO})]$ and $[\text{WCp}_2(\text{CO})]$ are both thermally stable, whereas formation of $[\text{CrCp}_2(\text{CO})]$ from CrCp_2 and CO is reversible with $\Delta H^\circ = 79.1$ kJ mol^{-1} and $\Delta S^\circ = -60$ $\text{J K}^{-1} \text{mol}^{-1}$. Formation of CrCp_2 ammonia adducts is also reversible.⁶ Tungstenocene is capable of forming a stable dicarbonyl species, although this retains an 18 electron structure by adopting a $[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_5\text{H}_5)_2(\text{CO})_2]$ conformation.⁷ The lower stability of $[\text{CrCp}_2(\text{CO})]$ has been attributed to the higher spin pairing energy for chromium on forming the singlet carbonyl complex from the triplet chromocene.^{5,8}

It was later shown that a stable chromocene carbonyl complex may be formed by bridging the cyclopentadienyl rings with a tetramethylethylene bridge.⁹ Comparison of the $\nu(\text{CO})$ frequencies of the unbridged and bridged carbonyl complexes (1900 and 1905 cm^{-1} respectively) suggests very similar degrees of back bonding from the metal implying little difference in M–CO bond strength. The stability of $[\text{Cr}\{\text{C}_2\text{Me}_4(\eta\text{-C}_5\text{H}_4)_2\}(\text{CO})]$ was therefore attributed to the fixation of the ligand framework by the interannular bridge. Further work by Simpson *et al.*¹⁰ suggested the stability of the *ansa*-chromocene CO adduct is due entirely to the bending of the ground state geometry and that any inductive effects of the *ansa*-linkage are minimal. *Ab initio* calculations showed the energy required to bend triplet chromocene from planar to the 143.3° observed in the CO adduct was 76 kJ mol^{-1} and that this value is half electronic and half steric ring–ring repulsion introduced on

bending. These arguments about the effect of an *ansa*-bridge are supported by the observation that the silicon bridged species $[\text{Cr}\{\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\}(\text{CO})]$ is also stable to thermolysis, showing no change in the ^1H NMR spectrum after 10 d at 60 °C.¹¹

The relative stabilities of the unbridged and *ansa*-chromocene carbonyls bear comparison with the thermal stabilities of unbridged and *ansa*-tungstenocene methyl hydrides. The unbridged species loses methane at 48 °C¹² whereas the methylene bridged analogue is stable up to 120 °C.¹³ The thermal stability of the *ansa*-bridged compound has been shown to be due to the steric constraint of the bridge stopping formation of a triplet tungstenocene with parallel rings.^{14,15}

The success of previous theoretical work on this latter system suggests that density functional calculations should provide a useful method for quantifying the energetics of the thermal stability of the Group 6 metallocene monocarbonyls. We report here dissociation energies for the Group 6 metallocene monocarbonyl complexes discussed above.

Computational methods

Calculations were performed using density functional methods of the Amsterdam Density Functional (ADF) package (Version 2.3).¹⁶ The electronic configurations were described by an uncontracted triple- ζ basis set of Slater type orbitals, with a single polarisation functional added; 2p on hydrogen and 3d on carbon and oxygen atoms. The cores of the atoms were frozen, carbon and oxygen up to the 1s, chromium to the 2p, molybdenum to the 3d, and tungsten to the 5p. First order relativistic corrections were made to the cores of all atoms using the Pauli formalism. Energies were calculated using the VWN (Vosko, Wilk, Nusair)¹⁷ local exchange correlation, with non-local exchange corrections by Becke,¹⁸ and non-local correlation corrections by Perdew.¹⁹ The non-local correction terms were not utilised in calculating gradients during geometry optimisations. This has been shown to be both computationally efficient and improves metal–ligand bond distances.²⁰

As it is not possible, within the ADF package to perform

Table 1 Calculations performed in this work (GO = geometry optimisation, SP = single point, F = frequency)

Calculation	Structure	Symmetry	Spin
GO, F	[CrCp ₂ (CO)]	C _{2v}	Singlet
GO, F		None	Singlet
GO, F	[MoCp ₂ (CO)]	C _{2v}	Singlet
GO, F	[WCp ₂ (CO)]	C _{2v}	Singlet
GO, F		None	Singlet
GO	[Cr{C ₂ H ₄ (C ₅ H ₄) ₂ }(CO)]	C ₂	Singlet
GO	CrCp ₂	C _{2v}	Singlet
GO		C _{2v}	Triplet
GO		D _{5h}	Triplet
GO	MoCp ₂	C _{2v}	Singlet
GO		C _{2v}	Triplet
GO		D _{5h}	Triplet
GO	WCp ₂	C _{2v}	Singlet
GO		C _{2v}	Triplet
GO		D _{5h}	Triplet
SP		D _{5h}	Spin-orbit
SP		C _{2v}	Spin-orbit
GO	CO	D _{5h}	Singlet

geometry optimisations under double point group symmetry, single-point spin-orbit calculations were performed on the optimised C_{2v} and D_{5h} triplet tungstenocene species using a formalism developed by Snijders *et al.*²¹

A summary of the calculations carried out is given in Table 1.

Results and discussion

Reaction energies for CO dissociation were estimated by optimising the geometries of the reactants and products and calculating the energy difference for the gas phase reaction (1)



(M = Cr, Mo or W). In order to elucidate the reasons for the differences in stability, the structures of the free metallocenes, MCp₂, were optimised in both a singlet and a triplet state for each metal.

Ground state structures

Geometry optimisations of [CrCp₂(CO)], [MoCp₂(CO)] and [WCp₂(CO)] under C_{2v} symmetry constraints all found minima on this surface. However, frequency calculations on these species gave very low imaginary frequencies corresponding to a slight antisymmetric twisting of the Cp ligands around their C₅ axes. The chromium and tungsten species also gave an imaginary frequency due to a bending of the W–C–O from the expected linear geometry. Further geometry optimisations were thus performed on [CrCp₂(CO)] and [WCp₂(CO)] with no symmetry constraints; frequency calculations on these structures had only positive frequencies showing that these were local minima on the energy surface. The final optimised structures are shown in Fig. 1 and structural parameters are presented in Table 2.

The C–O distances and the inter-ring angles are very similar for all three compounds suggesting bonding does not vary greatly down the Group. This view is supported by data from the frequency calculations where $\nu(\text{CO})$ is at 1945, 1965 and 1953 cm⁻¹ for [CrCp₂(CO)], [MoCp₂(CO)] and [WCp₂(CO)], respectively. The experimental values are 1900, 1921 and 1922 cm⁻¹ respectively.⁵ Fig. 2(a) shows schematic representations of the two highest occupied orbitals (3a₁ and 2b₁) and the two lowest unoccupied orbitals (3b₂ and 4a₁) in the metallocene carbonyls. It may be noted that the 2b₁ orbital is M–CO back bonding whereas the 3b₂ and 4a₁ orbitals are antibonding.

Geometry optimisations of the free metallocenes in the singlet state were carried out under C_{2v} symmetry constraints. These

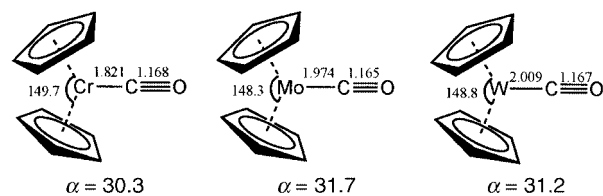


Fig. 1 Optimised geometries of bis(cyclopentadienyl) Group 6 carbonyls (α is the angle between the ring planes).

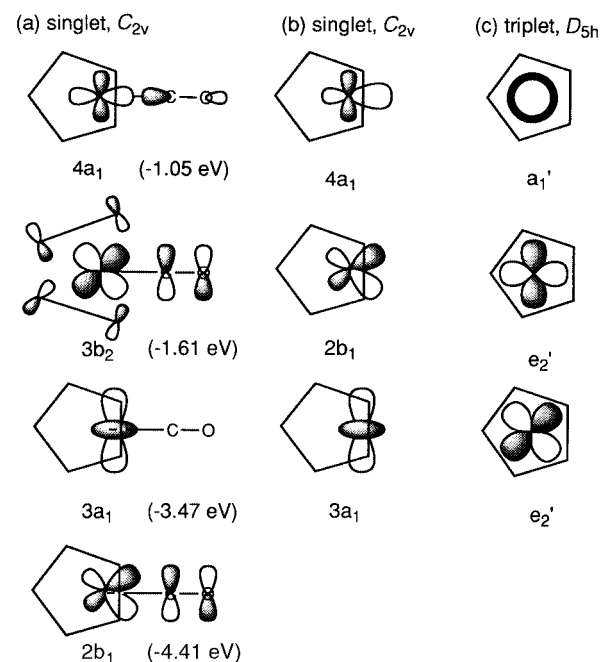


Fig. 2 Schematic representations of the frontier orbitals of (a) C_{2v} [MCp₂CO], (b) singlet C_{2v} MCp₂ and (c) triplet D_{5h} MCp₂.

gave bent structures for all three metallocenes with inter-ring angles varying from 27 to 32°. The ring angles are very similar to those calculated for the metallocene monocarbonyls suggesting that there is little steric repulsion between the rings on forming the monocarbonyl. Geometry convergence was only possible for CrCp₂ by lessening the SCF constraints within each cycle. The last cycle gave SCF convergence to a value of 2.9×10^{-5} . Structural parameters are presented in Table 2, and show little difference between the three structures. These d⁴ metallocenes in the singlet state have the d electrons occupying the 3a₁ and 2b₁ orbitals and avoid occupancy of the high lying 4a₁ orbital (Fig. 2b). They consequently bend significantly as this enables tighter binding of the rings.¹⁵

It has been long known that the ground state electronic structure of chromocene is ³E₂. Infrared and UV matrix isolation studies¹ have shown the structures of chromocene and molybdenocene to be distorted from a parallel ring structure by a Jahn–Teller effect. Interestingly, the crystal structure of chromocene shows the rings to be parallel.²² Conversely, tungstenocene does adopt a parallel ring structure²³ due to spin-orbit quenching of the distortion as is common with other tungsten complexes.²⁴ The ADF package has no implementation for modelling the spin-orbit effects within a geometry optimisation, so all three metallocenes were optimised under both D_{5h} and C_{2v} symmetry constraints in the triplet state. In all cases the Jahn–Teller distorted C_{2v} structures were lower lying in energy than the D_{5h} structures. Ring angles in these cases varied from 8 to 10°. Structural parameters are presented in Table 2. Single point calculations on the optimised C_{2v} and D_{5h} structures of Cp₂W with spin-orbit corrections showed the D_{5h} structure to be the lower in energy by 0.016

Table 2 Parameters for optimised structures of [MCp₂(CO)], [Cr{C₂H₄(η-C₅H₄)₂}(CO)], MCp₂ (M = Cr, Mo or W) and Cr[C₂H₄(η-C₅H₄)₂]

Compound	Constraint	Bond length/Å				<i>a</i> , Inter-ring angle ^a /°	M–C–O/°
		M–C	C–O	M–C _{ring}	C–C		
[CrCp ₂ (CO)]	Singlet no sym.	1.821	1.168	2.112–2.127	1.411–1.438	30.3	179.9
[MoCp ₂ (CO)]	Singlet C _{2v}	1.974	1.165	2.241–2.272	1.413–1.437	31.7	180
[WCp ₂ (CO)]	Singlet no sym.	2.009	1.167	2.300–2.330	1.416–1.434	31.2	179.2
CrCp ₂	Singlet C _{2v}	na	na	2.075–2.081	1.419–1.438	26.8	na
MoCp ₂	Singlet C _{2v}	na	na	2.193–2.242	1.421–1.440	31.8	na
WCp ₂	Singlet C _{2v}	na	na	2.223–2.294	1.423–1.444	32.1	na
CrCp ₂	Triplet C _{2v}	na	na	2.062–2.173	1.411–1.434	9.8	na
MoCp ₂	Triplet C _{2v}	na	na	2.219–2.320	1.413–1.433	8.2	na
WCp ₂	Triplet C _{2v}	na	na	2.258–2.380	1.412–1.435	9.1	na
CrCp ₂	Triplet D _{5h}	na	na	2.123	1.423	0	na
MoCp ₂	Triplet D _{5h}	na	na	2.276	1.423	0	na
WCp ₂	Triplet D _{5h}	na	na	2.325	1.424	0	na
[Cr{C ₂ H ₄ (η-C ₅ H ₄) ₂ }(CO)]	Singlet C ₂	1.830	1.167	2.109–2.137	1.409–1.436	35.4	180.0
[Cr{C ₂ Me ₄ (η-C ₅ H ₄) ₂ }(CO)] (crystal structure)		1.85	1.16	2.13–2.18	1.40–1.47	38.5	180.0
Cr[C ₂ H ₄ (η-C ₅ H ₄) ₂]	Singlet C ₂	na	na	2.058–2.095	1.416–1.437	35.0	na
Cr[C ₂ H ₄ (η-C ₅ H ₄) ₂]	Triplet C ₂	na	na	2.027–2.207	1.411–1.438	35.9	na

^a Defined as the angle between the planes of the cyclopentadienyl rings.

Table 3 Bond dissociation energies (kJ mol⁻¹) for loss of CO from [MCp₂(CO)]

Compound	To C _{2v} singlet	To C _{2v} triplet	To D _{5h} triplet
[CrCp ₂ (CO)]	222.0	76.4	99.3
[MoCp ₂ (CO)]	232.3	163.6	185.9
[WCp ₂ (CO)]	247.3	172.3	194.0
[Cr{C ₂ H ₄ (C ₅ H ₄) ₂ }(CO)]	226.5	112.1	na

eV (1.54 kJ mol⁻¹) consistent with the quenching of the Jahn–Teller distortion. This is consistent with an (e₂')³(a₁')¹ configuration (Fig. 2c).

Reaction thermodynamics

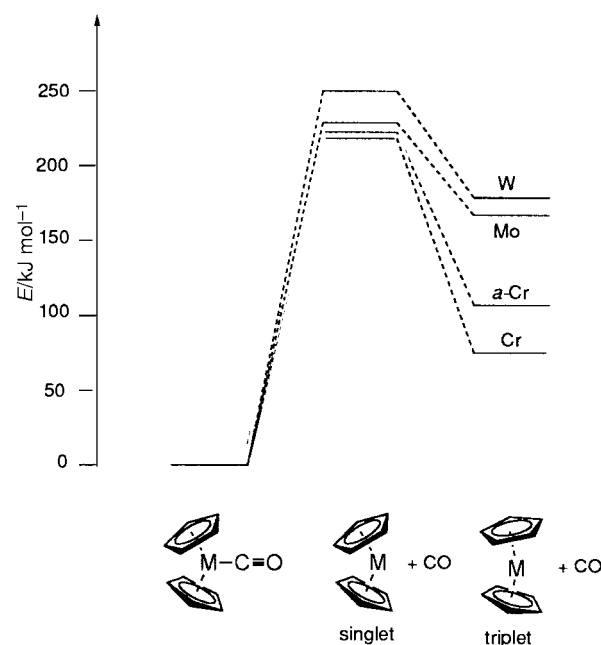
Given that the structures of the Group 6 metallocene carbonyls show neither significant deviation in geometry nor vibrational structure, it is likely, as Brintzinger deduced, that the different patterns of reactivity observed arise from differing stabilities of the free metallocenes. The dissociation energies to the various metallocene species are summarised in Table 3.

The bond dissociation energies for loss of CO from the carbonyl to give the singlet metallocene species and CO are 2.301 (Cr), 2.408 (Mo), and 2.563 (W) eV (222.0, 232.3, and 247.3 kJ mol⁻¹). This shows a typical increase in energy down the Group, but is not significant enough to explain the low thermal stability of [CrCp₂(CO)].

The triplet structures also show no significant differences in geometry. However, the bond dissociation energy for loss of CO to these species is significantly lower for chromium than for the lower Group 6 metals.

For all Group 6 metals the triplet metallocene species lies much lower than the singlet. Triplet chromocene lies 1.509 eV (145.6 kJ mol⁻¹) below the singlet. The difference is also significant for molybdenocene, 0.712 eV (68.7 kJ mol⁻¹), and tungstenocene, 0.777 eV (75.0 kJ mol⁻¹). The decrease in the relative stability of the triplet state on descending the Group is a consequence of the decrease in electron–electron repulsion with increasing principal quantum number.

The bond dissociation energies are estimated as 76 (Cr), 164 (Mo) and 172 kJ mol⁻¹ (W); the value for Cr is close to the experimental value of Δ*H*₀ of 79.1 kJ mol⁻¹. They are represented diagrammatically in Fig. 3, which gives a Born–Haber analysis of the energetics of the dissociation of CO from the bis(cyclopentadienyl) metal carbonyl in two stages. First there

**Fig. 3** Calculated CO dissociation energies of Group 6 metallocene monocarbonyls to singlet and triplet metallocenes and CO.

is the dissociation of CO from the metal carbonyl to yield the singlet metallocene and free CO. The singlet metallocene is then converted into the triplet state, which entails promotion of one electron into the 4a₁ LUMO, unpairing of the spins and the consequential relaxation of the rings to the favoured near-parallel ring geometry. This term is negative as electron–electron repulsions in the HOMO are relieved by promoting one electron to a spatially different orbital. The change in inter-ring angle occurs because the HOMO is antibonding when the metallocene is bent and becomes non-bonding when the rings are parallel.¹⁵ Since the orbitals on chromium are smaller than those of the lower Group 6 metals, there is a greater stabilisation possible on adoption of the triplet state, *i.e.* Cr has a greater pairing energy. It is this that causes [CrCp₂(CO)] to have such low stability.

The actual thermal reaction surface will involve a singlet–triplet crossing at some point as the M–C distance increases as was found for the elimination of methane from [WCp₂(Me)H].¹⁴

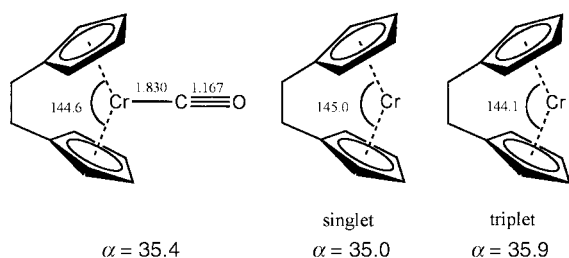


Fig. 4 Optimised structures of *ansa*-metallocene (α is the angle between the ring planes).

Effect of an *ansa* bridge

Brintzinger and co-workers⁹ have shown $[\text{Cr}\{\text{C}_2\text{Me}_4(\text{C}_5\text{H}_4)_2\}(\text{CO})]$ is thermally stable, unlike its non-bridged analogue. In order to test whether a quenching of the ring relaxation lessens the energy of the conversion into the triplet state, further calculations were carried out on the *ansa*-ethylene bridged system. Geometry optimisations performed on $[\text{Cr}\{\text{C}_2\text{H}_4(\text{C}_5\text{H}_4)_2\}(\text{CO})]$, singlet $\text{Cr}[\text{C}_2\text{H}_4(\text{C}_5\text{H}_4)_2]$ and triplet $\text{Cr}[\text{C}_2\text{H}_4(\text{C}_5\text{H}_4)_2]$ yielded structures presented in Table 2 and Fig. 4. The structure of the carbonyl complex is compared with the crystal structure of $[\text{Cr}\{\text{C}_2\text{Me}_4(\text{C}_5\text{H}_4)_2\}(\text{CO})]$ in Table 2.

It can be seen that the structural parameters calculated for $[\text{Cr}\{\text{C}_2\text{H}_4(\text{C}_5\text{H}_4)_2\}(\text{CO})]$ closely resemble those calculated for $[\text{CrCp}_2(\text{CO})]$. Notably, the ring angle differs by only 5.1° . The bridge, however, holds the rings at an angle of 35° and the triplet chromocene is unable to adopt its favoured angle of 10° . The triplet state is still the more stable but only by 1.185 eV (114.3 kJ mol^{-1}). This is reflected in the dissociation energies for loss of CO. These vary little to the singlet metallocene being 2.347 and 2.301 eV for ethylene bridged and non-bridged compounds respectively. To the triplet metallocenes the dissociation energies differ significantly being 1.162 and 0.792 eV (112.1 and 76.4 kJ mol^{-1}). This difference is sufficient to explain the thermal stability of $[\text{Cr}\{\text{C}_2\text{Me}_4(\text{C}_5\text{H}_4)_2\}(\text{CO})]$ at ambient temperatures.

Conclusion

The thermal stability of the heavier bis(cyclopentadienyl) Group 6 monocarbonyls is attributed to their inability to form a low energy metallocene product. Conversely, the thermal instability of $[\text{CrCp}_2(\text{CO})]$ is attributed to the ready formation of triplet chromocene, with the larger pairing energy for Cr compared to Mo and W creating an enthalpically more accessible product. However, the stabilisation gained on adopting the triplet state with its near-parallel ring geometry may be quenched by the introduction of an *ansa*-bridge which hinders formation of the optimum triplet state geometry.

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