

Modified Reactivity via Distortion of Ground-State Structure: Stability of Chromocene Carbonyls

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Summary: We show that the increased stability of the CO adduct of chromocene induced by incorporation of a two-carbon linker between the cyclopentadienyl rings is entirely due to distortion of the ground-state geometry. The distortional contribution factors equally between raising frontier orbital energies and eliminating ring-ring repulsive forces. It is clear that there is no contribution from an alkyl inductive effect.

Ring-bridged analogs of metallocenes, besides exhibiting the obvious ring-metal-ring bending structural distortion, generally differ from their unbridged parents in reactivity patterns. Smith and Brintzinger have reported that titanocenophanes do not form the dinitrogen and hydrido derivatives characteristic of titanocene itself, presumably due to restricted ring mobility.¹ Marks and co-workers have used bridging Cp groups to stabilize bis(cyclopentadienyl)uranium(IV) halide systems with respect to ligand redistribution.² Manganocenophane forms only a mono(pyridine) adduct while manganocene forms both mono- and bis(pyridine) adducts, once again due to steric constraints.³

In contrast, while chromocene binds CO very weakly,⁴ incorporation of a heteroannular ethylene bridge promotes formation of a robustly stable CO adduct.⁵ It is this result we wish to address.

The origin of this enhanced stability could be perceived to be due to (a) electronic effects emanating from ring substitution, (b) electronic effects due to changes in frontier orbital energies which accompany the bending back of the rings, and (c) elimination of the steric penalty incurred during the bending back of rings which derives from ring-ring nonbonded repulsions. We have attempted to factor these three effects via equilibration of CO with a model system and calculation of distortional energetics using both classical and quantum mechanical approaches.

Results and Discussion

Thermodynamic Stability of a Ring-Substituted Chromocene Carbonyl Complex. The thermodynamics of the reaction between dimethylchromocene ((CH₃C₅H₄)₂Cr) and carbon monoxide were examined in order to experimentally determine the effect of alkyl group substitution on the stability of Brintzinger's tetramethyl-ethylene-bridged chromocene carbonyl complex.⁵ Our determination of the enthalpy and entropy of complex formation for (η⁵-CH₃C₅H₄)₂CrCO and comparison with data for Cp₂CrCO allows one to specify the alkyl group inductive effect.

Table I presents the data obtained from measurements of the equilibrium pressure of CO over a partially carbo-

Table I. Equilibrium Data^a for the Reaction
(η⁵-CH₃C₅H₄)₂Cr(sol) + CO(g) ↔ (η⁵-CH₃C₅H₄)₂CrCO(sol)

T, K	P _{CO} , Torr	K, atm ⁻¹	T, K	P _{CO} , Torr	K, atm ⁻¹
273	3.1	130	297	24.9	10.8
277	6.0	63.6	303	35.3	6.11
285	11.3	30.6			

^a In toluene as solvent.

Table II. STO-3G Unoptimized Energies for the Cr(Cp)₂ System

structure ^a	energies, hartrees	structure ^a	energies, hartrees
ground state (triplet)	-1412.18504	CO adduct	-1523.41495
bent (triplet)	-1412.15169	CO	-111.21205

^a Structural parameters are as follows. Cp Ring: C-C, 1.419 Å; C-H, 1.076 Å; H's bent toward metal by 2.8°. Metal complex: symmetrical, Cr-Cp ring center = 1.802 Å; bent, Cr-Cp ring center = 1.84 Å and ring-Cr-ring = 143.3°; CO adduct, as in the bent form plus Cr-CO = 1.89 Å and C-O = 1.16 Å.

nylated dimethylchromocene solution in toluene. The data reduces to a standard enthalpy for complex formation of -16.1 ± 0.8 kcal·mol⁻¹ and a standard entropy of -50 ± 3 cal·mol⁻¹·K⁻¹. In comparison, the ΔH° and ΔS° values for formation of Cp₂CrCO in toluene reported by Brintzinger et al. are -18.8 ± 0.5 kcal·mol⁻¹ and -60 ± 2 cal·mol⁻¹·K⁻¹, respectively.⁴ These data indicate that there is little, if any, influence on the stability of the bridged chromocene carbonyl through the inductive effect of the bridge alkyl groups.

Bending Chromocene. The penalty inherent in bending the ring-metal-ring angle from the linear geometry observed for chromocene to the 143.3° value observed for the chromocenophane CO adduct⁴ was estimated from both classical mechanical and quantum mechanical perspectives. In all cases we use the eclipsed *D*_{5h} symmetry undistorted sandwich as a reference point.

In the classical approach we began by using the experimental value⁶ for the diagonal harmonic ring-metal-ring bending vibration (ν_{22}) of 0.3 mdyne-radian⁻² to estimate the final potential energy of the bent system but soon realized that, for such a large distortion, nonbonded repulsions between closely approaching cyclopentadienyl ring hydrogens and carbons were substantial. Thus, the penalty for bending was calculated as

$$E_{\text{bend}} = \frac{1}{2}k_{\text{bend}}(\Delta\theta)^2 + \sum E_{\text{van der Waals}}$$

A variety of parameter sets for the van der Waals parameters were explored⁷ with the outcome that although the nonbonded ring-ring repulsion factored differently (between H...H, C...C, and H...C atom pairs; plus in the case of the MM3 force field C-H dipole-dipole interactions), the penalty of ca. 18 ± 2 kcal·mol⁻¹ for bending to final

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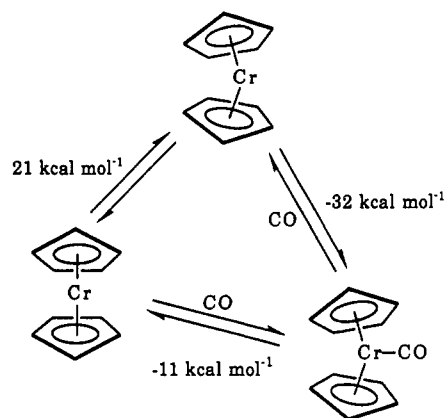


Figure 1. Model reaction sequence for carbonylation of $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Cr}$. Values shown are the standard enthalpies of reaction calculated by SPARTAN.⁹ See Table II for reference energies.

geometry was quite constant. Also this energy factored ca. 50/50 between contributions from the bending and ring-ring repulsion terms. The bending energy is quite asymmetrical, with the direction which brings a carbon pair into close proximity exacting a larger penalty than bending in the opposite direction to bring two ring edges together.⁸

Next we designed a model reaction sequence in which chromocene was first bent and then carbonylated. This was quantitatively evaluated at the STO-3G level of theory using the program SPARTAN⁹ (Table II). We felt this was necessary because while the classical, unlike the quantum mechanical, model allows for factoring of electronic and steric contributions to bending (an artificial concept quantum mechanically), it cannot address the metal-ligand coupling step. The total energy for bending was once again in the vicinity of 20 kcal·mol⁻¹ (21 kcal·mol⁻¹). But now the bending and metal-ligand bond-forming steps can be factored as shown in Figure 1. We note that an extended Huckel calculation by Brintzinger et al.¹⁰ gave a very similar energy for bending chromocene.

Thus we conclude that the advantage of [2]chromocenophane over chromocene in stability of the CO adduct is entirely due to bending of the ground-state geometry, with minimal contribution from any alkyl inductive effect. Retaining the classical concept of sterics, we find that the

advantage is about half steric and half electronic, with the electronic contribution coming from prior raising of frontier orbital energies.

Experimental Section

General Procedures. Reagent grade toluene was purified by distillation from sodium-benzophenone ketyl and was stored under argon. Carbon monoxide (Matheson, 99% purity) was purified by passage through a toluene solution of sodium-benzophenone ketyl and a series of dry ice traps. Dimethylchromocene was prepared by a literature method.¹¹ Argon and nitrogen were purified by passage through BASF R3-11 catalyst to remove oxygen and the P₄O₁₀-based dessicant Aquasorb (Mallinckrodt) to remove water.

Air-sensitive solids were stored and manipulated under nitrogen in a Vacuum Atmospheres inert-atmosphere glovebox. Air-sensitive solutions and dry, deoxygenated solvents were transferred under argon through stainless steel cannulas. All reactions were carried out under argon using standard inert-atmosphere and Schlenk techniques.

Equilibrium Measurements for $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Cr} + \text{CO} \rightleftharpoons (\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})$. Dimethylchromocene (386 mg, 1.84 mmol) was dissolved in 25 mL of toluene in a flask of known volume. The flask was connected to a vacuum manifold of known volume and cooled to -78 °C, and CO gas (0.663 mmol) was introduced and allowed to react with the dimethylchromocene at this temperature. The system was maintained at various temperatures by use of a cryostatic bath and the total pressure measured manometrically. By correction for the vapor pressure of the solvent, the equilibrium pressure of CO, P_{CO} , was obtained. The equilibrium constant at each temperature was determined from the expression

$$K = \frac{[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Cr}(\text{CO})]}{[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Cr}]P_{\text{CO}}} = \frac{N^{\circ}\text{CO} - N_{\text{CO}}}{(N_{(\text{MeCp})_2\text{Cr}} - N^{\circ}\text{CO} - N_{\text{CO}})P_{\text{CO}}}$$

where $N^{\circ}\text{CO}$ is the number of millimoles of CO introduced into the system and $N_{(\text{MeCp})_2\text{Cr}}$ is the number of millimoles of $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Cr}$ prior to reaction with CO. N_{CO} , the number of millimoles of CO in the gas phase, was determined from the ideal gas law. Values of the equilibrium constant K (atm⁻¹) for the reaction are given in Table I. These data were fit to the equation of a straight line by a least-squares program to obtain ΔH° and ΔS° for the carbonylation reaction.

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Registry No. Chromocene, 1271-24-5; 1,1'-dimethylchromocene, 12146-92-8.

OM920341O

(8) The results for the MM3 force field are E (kcal/mol) = $17.33\theta^2 - 2.09\theta^3 + 44.25\theta^4 - 9.09\theta^5$, where the angle θ , in radians, represents the deviation of the ring center-metal-ring center angle from 180° and is negative when the eclipsed form of the metallocene is bent so that one carbon from each ring becomes the closest point of approach.

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