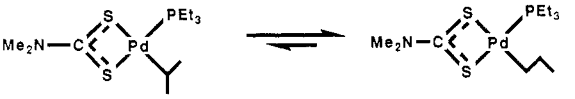
both R′ = Et and R′ = Ph and are also extremely thermally stable. They can be heated at 130 °C for extended periods with no measurable decomposition.

(1)

(2)

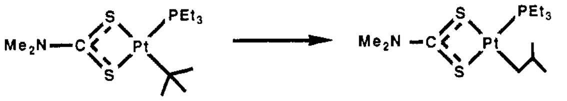
(3)



(4)

At these elevated temperatures, the alkyl complexes undergo a slow isomerization reaction ($t_{1/2}$ of ca. 8 h at 130 °C for platinum and 5 h at 75 °C for palladium) of the alkyl ligand in aromatic solvents (eqs 1–4). In all cases, both isomers have been prepared directly and equilibrate to the mixtures shown. The positions of the isomerization equilibria at 120 °C are 9/1.0 (primary/secondary isomer) for all three of the platinum cases.[13] For the palladium reaction it is 10/1.0 at 75 °C. As expected, the isomer with the metal bonded to a primary carbon is favored, but substantial amounts of the secondary isomer are present in the equilibrium mixtures. In the platinum system, substituting PEt$_3$ with the sterically more demanding PPh$_3$ ligand or changing the alkyl ligand from propyl to the sterically larger butyl ligand has little effect on the ratio of secondary/primary isomer. This indicates that the equilibria are not greatly influenced by steric contributions from the dithiocarbamate and phosphine ligands. The lack of steric crowding by the ancillary ligands has been verified crystallographically.[14] The 9/1.0 ratio of primary to secondary alkyl isomers for platinum at 120 °C is a free energy difference of 1.7 kcal/mol, while the 10/1.0 ratio for palladium at 75 °C is 1.6 kcal/mol. We believe that this represents the bond energy difference in primary versus secondary alkyls for these metals in the absence of steric constraints imposed by other ligands in the coordination sphere. Other estimations of these differences contain both steric and electronic contributions and are generally at least 5 kcal/mol.[15] For comparison, the energy difference in a C–H bond for primary versus secondary carbon atoms is ca. 3 kcal/mol.[16] The lower value for the transition-metal complexes may simply reflect the longer M–C bond distances, although other factors such as electronegativity differences could also be important.

The *tert*-butyl complex, [Me$_2$NCS$_2$]Pt(PEt$_3$)(*t*-Bu), has also been prepared. It is also unusually stable but completely isomerizes to the primary isomer at 120 °C (eq 5).



(5)

Thus, the energy difference for a primary over a tertiary metal–carbon bond must be at least 4 kcal/mol.

Only a limited number of isomerization reactions of this type have been investigated previously. Our observations of substantial amounts of secondary carbon isomers at equilibrium are contrasted by the fact that in the CpFeCO(PPh$_3$)(alkyl),[3] IrZI(CO)L$_2$(alkyl) (Z = Cl, I; L = PMe$_3$, PMe$_2$Ph),[4d] and RIrCl$_2$(CO)(PPh$_3$)$_2$[4a,c] systems the secondary isomers rearrange completely to the primary isomers. In these systems, a significant contribution to the position of the isomerization reaction is expected from the steric effects of the bulky ancillary ligands, an effect clearly favoring the primary isomers. A similar result is observed with *cis*-Pt(PPh$_3$)$_2$Et(alkyl) complexes.[5] Although this case is somewhat similar to the system being studied here, the cis phosphines are sterically bulky and will influence the equilibrium position. Only in the dimeric system [Ir(CO)$_2$Cl(μ-Cl)R]$_2$, which was described as having low steric constraints, were substantial amounts of both primary and secondary isomers noted.[4b] Also, *trans*-(*t*-Bu)Me$_2$AuPPh$_3$ isomerizes completely to *trans*-(*i*-Bu)Me$_2$AuPPh$_3$.[6]

The platinum and palladium system outlined here is designed to study the isomerization of an alkyl ligand by systematically varying the metal, the phosphine ligand, and the alkyl ligand itself. We plan to study electronic and steric effects on the stability of the alkylmetal isomers by further varying these groups. This is fundamental information in many catalytic processes, such as the hydroformylation reaction, that involve alkylmetal intermediates.[1]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also partially supported by a grant from the University of South Carolina Venture Fund. The NSF (Grant Nos. CHE-8411172 and CHE-8904942) and NIH (Grant No. RR-02425) have supplied funds to support NMR equipment, and the NIH (Grant RR-02849) has supplied funds to support mass spectrometry equipment.

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(13) The positions of the equilibria were determined by ^{31}P NMR spectroscopy with use of sealed tubes in which the solution had been degassed by freeze–thaw pumping sequences. The resonance for each isomer had base-line separation, and the pulsing sequence was carefully checked for saturation. The digital resolution was 0.037 Hz/point with a minimum width at half-height of 0.4 Hz. The signal to noise ratios on the smaller resonance were greater than 100/1. An exception in which the signal to noise ratio was ca. 8/1 was the [Me$_2$NCS$_2$]Pt(PPh$_3$)(Bu) mixture (eq 3), for which the equilibrium ratio had to be determined from the upfield platinum satellites in order to achieve base-line resolution.

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Contribution of Olefinic Ring Strain to (CO)$_5$Cr–Cyclooctene Bond Strengths

Jane K. Klassen and Gilbert K. Yang*

Department of Chemistry, University of Southern California
Los Angeles, California 90089-0744

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Summary: The Cr–olefin bond in Cr(CO)$_5$(cyclooctene) complexes was found to be 5 kcal/mol stronger for *trans*-cyclooctene than for *cis*-cyclooctene. The similarity of the rates of reaction of photochemically generated Cr(CO)$_5$S with free *cis*- or *trans*-cyclooctene suggests that steric factors contribute little to this difference.

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* To whom correspondence should be addressed.

Scheme I

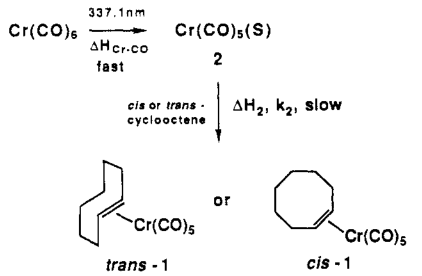

Table I. Enthalpic and Kinetic Data for Reactions of 2 with Olefins in Heptane Solution[a]

ligand	ΔH_{Cr-CO}, kcal/mol	ΔH_2, kcal/mol	k_2, 10^7 L/(mol s)	source
cis-cyclooctene	27.8 ± 1.6	−14.3 ± 0.9	1.4 ± 0.3	this work
trans-cyclooctene	27.7 ± 1.9	−19.5 ± 2.5	1.7 ± 0.2	this work
1-hexene	27.0 ± 1.2	−12.2 ± 1.2	3.0 ± 1.5	ref 7c

[a] Errors are given as 1 standard deviation of the scatter in the data.

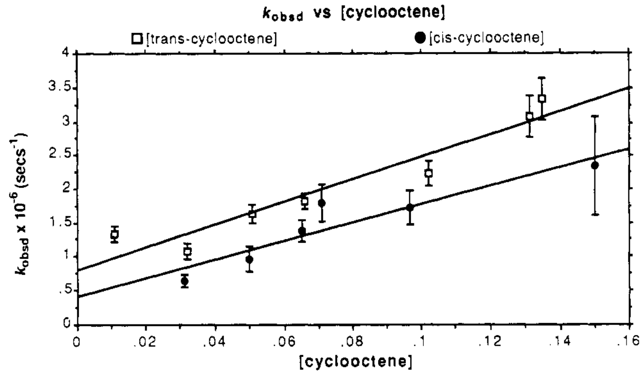

Figure 1. Plot of k_{obsd} vs [cyclooctene] for the reaction of $Cr(CO)_5S$ with *cis*- and *trans*-cyclooctene. For *cis*-cyclooctene, $r^2 = 0.92$. For *trans*-cyclooctene, $r^2 = 0.87$. Other data are given in Table I. Error bars are the greater of the standard deviation calculated from the scatter in each point or ±10%.

There are many examples of organometallic complexes that owe their stability, at least in part, to the relief of strain in the organic ligand. Transition-metal benzyne,[1] cyclohexyne,[2] and bicyclic bridgehead olefin[3] complexes are among these. The relative stability of transition-metal complexes of strained olefins over that of their unstrained counterparts has long been recognized,[3,4] and attempts have been made to determine the magnitude of this stabilization.[5] An example of this difference in relative stability is found in the chemistry of *cis*- and *trans*-cyclooctene.[6] Here, we report the determination of the metal–olefin bond dissociation energies in both $(CO)_5Cr$(*cis*-cyclooctene) (*cis*-1) and $(CO)_5Cr$(*trans*-cyclooctene) (*trans*-1) using time-resolved photoacoustic calorimetry.

Time-resolved photoacoustic calorimetry has been used to determine the enthalpies and quantum yields of reaction in inorganic and organic systems.[7] Our experimental technique is similar to those previously described in the literature.[7a] Emission from an N_2 laser (337.1 nm, 1-ns pulse length, 20 μJ/pulse) is passed through a quartz cuvette containing an argon-purged heptane solution of either *cis*- or *trans*-cyclooctene[8] and either a reference compound (ferrocene) or $Cr(CO)_6$ (ca. 10^{-3} M) at 25 ± 1 °C.[9] Absorbance values were matched to within 3%. The data yield the heats of reaction for "fast" processes ($k_{obsd} > 10^8$ s^{-1}) and "slow" processes (10^5 $s^{-1} < k_{obsd} < 10^7$ s^{-1}) and also yield the rate constant for the slower process.[10] The concentration of the cyclooctene was varied from ~0.03 to ~0.15 M, making it more than 10 times the concentration of $Cr(CO)_6$.[11] At least two determinations were performed at each concentration. No change in the measured enthalpies of reaction was observed over this concentration range. No laser energy dependence of the results was observed.[12]

Upon photolysis of $Cr(CO)_6$ in a hydrocarbon solution of either *cis*- or *trans*-cyclooctene, CO is lost in less than 100 ps[13] ("fast" step in Scheme I), forming the solvated $Cr(CO)_5S$ intermediate (2), which subsequently binds olefin in a second-order reaction (k_2 step in Scheme I) to form either *cis*-1 or *trans*-1.[6b] Both *cis*-1 and *trans*-1 have been isolated and characterized as distinct and different species.[6b] These two steps have rate constants that fit the "fast" and "slow" criteria demanded by the photoacoustic technique, allowing us to determine ΔH_{Cr-CO}, ΔH_2, and k_2. The results are summarized in Table I. The $(CO)_5Cr$–CO bond dissociation energy in heptane (ΔH_{Cr-CO}) of 27.8 ± 1.7 kcal/mol is in excellent agreement with that reported earlier for this reaction[7c,14] and is independent of both the structure and concentration of the cyclooctene used in the experiment.

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(9) Ferrocene and $Cr(CO)_6$ were sublimed prior to use; the cyclooctenes were pure as determined by ^1H NMR spectroscopy. Heptane was olefin-free as determined by GC (<50 ppm) and was used without purification.

(10) Deconvolution with a two-decay fit yielded excellent fits with a normalized $\sum r^2$ value less than 0.3%. No significant improvement was obtained by using a three-decay fit to the data.

(11) The concentration of $Cr(CO)_5$ is at least 1000 times smaller than $[Cr(CO)_6]$. Thus, the reactions are run under pseudo-first-order conditions with respect to the $Cr(CO)_5$ intermediate.

(12) The laser energy ranged from a minimum of 12 μJ/pulse to a maximum of 25 μJ/pulse with no difference in the results. This observation agrees with previous reports.[7c]

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(14) The difference between the solution and gas-phase Cr–CO bond dissociation energies has been attributed to the interaction between heptane and $Cr(CO)_5$.[7c]

The heat of reaction, ΔH_2, for the binding of *cis*-cyclooctene to the solvated intermediate **2** to generate *cis*-**1** was found to be −14.3 ± 0.9 kcal/mol. This is somewhat more exothermic than the −12.2 kcal/mol olefin–metal bond enthalpy found in (1-hexene)$Cr(CO)_5$.[7c] A much more dramatic effect is seen in the enthalpy of binding of *trans*-cyclooctene to intermediate **2**. In this case, $\Delta H_2 = -19.5 \pm 2.5$ kcal/mol. Thus, the metal–olefin bond in *trans*-**1** is more than 5 kcal/mol stronger than that in *cis*-**1**; i.e., $\Delta\Delta H_2 \approx 5$ kcal/mol.

Coordination of an olefin to a metal results in greater sp^3 hybridization at the olefinic carbons, the limiting case being formation of a metallacyclopropane complex.[15] If the hybridization change reduces strain by introducing greater flexibility into the olefin, then the metal–olefin interaction should be stronger.[3–6,15] Thus, our result that $\Delta\Delta H_2 \approx 5$ kcal/mol is consistent with the observation that *trans*-cyclooctene has ~10.4 kcal/mol of strain relative to *cis*-cyclooctene.[16,17] An estimate of the strain relief possible in the *cis*/*trans*-cyclooctene system is seen upon cyclopropanation of the double bond to form the corresponding *cis*- and *trans*-bicyclo[6.1.0]nonanes. The heats of formation of these two bicyclononanes differ by less than 1 kcal/mol.[18] Thus, while coordination of the cyclooctene double bond to $Cr(CO)_5$ relieves half of the strain associated with the trans double bond relative to the cis double bond, cyclopropanation relieves nearly *all* of this strain. In addition to rehybridization, different steric interactions may also contribute to $\Delta\Delta H_2$, although we believe that this effect is minimal (vide infra).

The rate of substitution of solvent in intermediate **2** by both *cis*- and *trans*-cyclooctene exhibited an apparent first-order dependence on the concentration of the cyclooctene. The data are plotted in Figure 1. The rates of these two substitution processes are nearly identical with second-order rate constants k_2 for *cis*- and *trans*-cyclooctene, respectively, of (1.4 ± 0.3) × 10^7 and (1.7 ± 0.2) × 10^7 L/(mol s) (Table I).[19] These rate constants are very similar to previously reported rate constants for reaction of intermediate **2** with a number of different ligands.[7c,20] From comparisons of the rates and enthalpies of reaction of α-methyl-substituted and unsubstituted pyridine and THF ligands with $Cr(CO)_5S$ in heptane solution, it is apparent that steric influences which have an effect on the enthalpy of reaction also have a substantial effect on the rate of reaction.[21] The lack of a substantial difference in the rate constants k_2 for *cis*- and *trans*-cyclooctene supports the conclusion that strain relief and not steric bulk is the primary component in $\Delta\Delta H_2$.

Acknowledgment. We acknowledge the National Institutes of Health (Grant No. GM-42704-01) and the donors of the Petroleum Research Fund, administered by the American Chemical Society for financial support of this research and Professor Tom Flood for helpful discussions.

Registry No. *trans*-1, 92937-36-5; *cis*-1, 92889-73-1.

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(15) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(16) This is the average of two values: 11.4 kcal/mol (Rogers, D. W.; von Voithenberg, H.; Allinger, N. L. *J. Org. Chem.* **1978**, *43*, 360–361) and 9.3 kcal/mol (Turner, R. B.; Meador, W. R. *J. Am. Chem. Soc.* **1957**, *79*, 4133–4136).

(17) Although crystallographic data are unavailable for complexes *cis*-1 and *trans*-1, ^{13}C NMR data confirm the greater sp^3 hybridization at the olefinic carbons in the trans complex compared to that in the cis complex.[6b] Further support for a substantial change in hybridization is found in comparison of X-ray data of the free *trans*-cyclooctene moiety to those of Fe-*trans*-cyclooctene complexes. The double-bond dihedral angle *decreases* from 138° in the free *trans*-cyclooctene structure to 125° upon complexation in $Fe(CO)_3$(*trans*-cyclooctene)$_2$. See ref 6c and: Ermer, O.; Mason, S. A. *Acta Crystallogr.* **1982**, *B38*, 2200–2206. Such a decrease in the dihedral angle must substantially reduce the strain inherent in the *trans*-cyclooctene moiety.

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(19) The apparent positive intercepts in Figure 1 may be due to reaction with impurities. Although the scatter in our data makes us wary of drawing any conclusions based on the *y* intercepts, this point deserves to be addressed. The only likely impurity in these experiments is water in the heptane. Given the low solubility of water in hydrocarbons (~3 mmol at 298 K; see: Goldman, S. *Can. J. Chem.* **1974**, *52*, 1668), water will have a noticeable effect on k_{obsd} only at the lower concentrations of cyclooctene (≲0.03 M). However, the rate constants k_2 are derived from the *slopes* of the plots in Figure 1, and therefore the values of k_2 we obtained are *not dependent* on reaction with an impurity in the solvent. Since the enthalpic data have no concentration dependence, the contribution of reaction with the impurity either is negligible or has an enthalpy of reaction very similar to that of the reactions being examined. We thank the reviewers for bringing up these points.

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(21) For example, in heptane solution, pyridine reacts with $Cr(CO)_5S$ more exothermically (2.3 kcal/mol) and faster (10 times) than does 2-picoline.[7c]

Cyclopentadiene Functionalization versus Fulvalene Formation in the Oxidation of $[(\eta^1{:}\eta^5\text{-}C_5H_4)ZrCp(PMe_3)]_2$: Preparation and Crystal Structures of $[(\eta^1{:}\eta^5\text{-}C_5H_4)ZrCp]_2[\mu\text{-}NSiMe_3]$ and $[(\eta^1{:}\eta^5\text{-}C_5H_4)][\mu\text{-}NSiMe_3][CpZrSPh][Cp(C_5H_4SPh)Zr]$

Ytsen Wielstra and Auke Meetsma

Laboratorium voor Anorganische Chemie
Rijksuniversiteit Groningen, Nijenborgh 16
9747 AG Groningen, The Netherlands

Sandro Gambarotta*

Chemistry Department, University of Ottawa
Ottawa, Ontario K1N 6N5, Canada

Saeed Khan

Department of Chemistry and Biochemistry
and Solid State Science Center, University of California
Los Angeles, California 90024

Received November 9, 1989

Summary: Oxidation of $[CpZr(PMe_3)(\eta^1{:}\eta^5\text{-}C_5H_4)]_2$ (**1**) by Me_3SiN_3 led to the formation of the dinuclear imido-bridged complex $[CpZr(\eta^1{:}\eta^5\text{-}C_5H_4)]_2(\mu\text{-}NSiMe_3)$ (**2**). Reaction of **2** with PhSSPh cleaved one of the two Zr–$(\eta^1{:}\eta^5\text{-}C_5H_4)$ bonds, forming the asymmetric dinuclear complex $[(\eta^1{:}\eta^5\text{-}C_5H_4)][\mu\text{-}NSiMe_3][CpZrSPh][Cp(C_5H_4SPh)Zr]$ (**3**). Crystal data for **2** and **3** are as follows: **2**, orthorhombic, space group $Pn2_1a$, a = 17.140 (1) Å, b = 24.973 (1) Å, c = 10.259 (1) Å, Z = 8, R = 0.032 (R_w = 0.040) for 2979 observed reflections; **3**, triclinic, space group $P\bar{1}$, a = 9.943 (1) Å, b = 10.742 (1) Å, c = 15.417 (2) Å, α = 75.736 (9)°, β = 79.58 (1)°, γ = 87.59 (1)°, Z = 2, R = 0.024 (R_w = 0.032) for 6572 observed reflections.

The most attractive characteristic of the fulvalene dianion as a ligand is its ability to enforce very short contacts between two metals (up to the metal–metal bond range),[1]

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(1) See for example: (a) Smart, J. C.; Curtis, C. J. *J. Am. Chem. Soc.* **1977**, *99*, 3518. (b) Gambarotta, S.; Chiang, M. Y. N. *Organometallics* **1987**, *6*, 897.

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