Table I. Oxidation and Reduction Potentials[a]

complex	solvent	$E_{1/2}$(ox), V	$E_{1/2}$(red), V
$Mo_2Cl_4(PMe_3)_4$	THF	0.74[b]	−1.70
	CH_2Cl_2	0.47	
$Mo_2Br_4(PMe_3)_4$	THF	0.87	−1.48
	CH_2Cl_2	0.59	
$Mo_2I_4(PMe_3)_4$	THF	0.88	−1.28
$Mo_2Cl_4(PEt_3)_4$	THF	0.67	−1.81
	CH_2Cl_2	0.35	
$Mo_2Br_4(PEt_3)_4$	THF	0.76[c]	−1.59[c]
$Mo_2Cl_4(PPr^n_3)_4$	THF	0.65	−1.89
	CH_2Cl_2	0.38	
$Mo_2Cl_4(PBu^n_3)_4$	THF	0.65	−2.00
	CH_2Cl_2	0.31	

[a] All potentials are referenced to the saturated calomel electrode (SCE); cyclic voltammograms were recorded in 0.1 M n-Bu_4NPF_6/THF at 25 °C. [b] See ref 4c. [c] The couples are irreversible at 25 °C; these data were taken at 0 °C. As a control, a cyclic voltammogram of $Mo_2Cl_4(PMe_3)_4$ was recorded at 0 °C; the shift in half-wave potentials is less than 50 mV.

is observed in THF and CH_2Cl_2 (Table I), which have different solvation properties. Furthermore, it is apparent that the IHO is not due to differences in metal–metal bond lengths (Δd is 0.005 (1) Å for the $Mo_2X_4(PMe_3)_4$ series).[7,8]

As the phosphine alkyl groups are changed from methyl to ethyl in the $Mo_2X_4(PR_3)_4$ dimers, the oxidation potential becomes less positive. Upon further lengthening of the alkyl chain, no large changes in $E_{1/2}$ (ox) are observed. The reduction potential, in contrast, is more negative by 100 mV for each methylene unit added to the chain. Although the origin of this shift is unknown,[9] it is clear that the halide dependence of this potential is not affected by the change in phosphine.[10]

One possible explanation of the IHO is metal (d)-to-halide (d) back-bonding,[11] because the Mo_2 unit in these molecules is especially electron-rich, and the back-bonding interaction should increase according to Cl < Br < I. The reduction potential (a function of the δ^* orbital energy) is more sensitive to the halide than the oxidation potential (which is a function of the δ orbital energy), indicating that the ligand orbitals interacting with the δ and δ^* levels are higher in energy than the metal based orbitals.

Walton and co-workers have shown that exchange of the halide for a moderate π-acceptor (NCS^-) makes the reduction potential of $Mo_2X_4(PEt_3)_4$ less negative, and the oxidation potential more positive,[4a] thereby implying that π-back-bonding interactions can be important in determining the redox properties of these systems. Walton's group also has studied a number of related rhenium dimers, whose redox properties[12] indicate that metal–halide back-bonding may be a factor in their electronic structures. Our view is that back-bonding to halide is important in the Re(II,II) dimers, where an IHO is observed.[12] When the Re_2 unit is less electron-rich [Re(II,III)], the back-bonding is diminished, which is evidenced by a normal order of redox potentials.

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(6) Reduction of these dimers was not observed in methylene chloride solution.

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(9) These changes in R have no influence on the $^1(\delta \rightarrow \delta^*)$ energy or intensity.[8]

(10) For example, the difference in reduction potentials between the chloride and bromide derivatives of both $Mo_2X_4(PMe_3)_4$ and $Mo_2X_4(PEt_3)_4$ is 0.22 V.

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Is Triquinacene Homoaromatic? A Thermochemical Answer in the Affirmative

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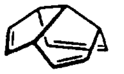
Aromaticity is a well-documented and multifaceted concept in organic chemistry. This is true for neutral and charged carbocycles alike. Homoaromaticity in ions is likewise documented, while in neutral species homoaromaticity has proven a great deal more elusive.[2] Numerous well-designed neutral species seem to lack the expected additional stabilization and some even have structural features suggestive of destabilization. We opt here for a thermochemical definition of aromaticity and homoaromaticity rather than one based on structural or spectroscopic features. More precisely, we ask if the species of interest with its array of conjugated (homoconjugated) double bonds is thermodynamically more stable than what would be derived from the properties of its nonconjugated (nonhomoconjugated) analogues? If so, the species is aromatic (homoaromatic). By this definition, benzene is aromatic because its heat of hydrogenation is less than 3 times that of cyclohexene. By this definition, *cis,cis,cis*-1,4,7-cyclononatriene is not homoaromatic because its heat of hydrogenation exceeds 3 times that of *cis*-cyclononene.[3] What about triquinacene[4] (**1**)? Our experiments, described briefly below, show that the heat of hydrogenation of this triene (−78.0 (± 0.5) kcal mol^{-1}) is less than 3 times that of the reference monoolefin, tetrahydrotriquinacene (**3**) (−27.5 (±0.3) kcal mol^{-1}) by 4.5 kcal mol^{-1}. These measurements show tetrahydrotriquinacene to be "normal" because its heat of hydrogenation is nearly exactly that suggested for cyclopentene[5] (−26.94 (±0.13) kcal mol^{-1}) and half of the value we found for the diene dihydrotriquinacene (**2**) (−55.0 (±0.4) kcal mol^{-1}). Accurate, but less conceptually relatable, experiments such as CD[6a] and PES[6b] set aside, it seems quite unambiguous that triquinacene enjoys a small but significant degree of homoaromaticity.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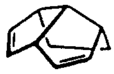
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Synthesis. Triquinacene and its di- and tetrahydro derivatives were synthesized as follows. **Triquinacene**: 2,3-Dihydrotriquinacen-2-one[7] was reduced with lithium aluminum hydride to the endo alcohol whose mesylate was subjected to E_2 elimination on activated alumina.[8] The spectral properties of the hydrocarbon, which was purified to the 100% level by preparative VPC (15 ft × 0.25 in. 10% SE-30 on Chromosorb W), were identical with those earlier reported. **Dihydrotriquinacene**: Lithium aluminum

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hydride reduction[6a] of the predescribed endomesylate provided the known dihydro derivative.[8,9] **Tetrahydrotriquinacene**: *exo*-9-Hydroxy-2,3,8,9-tetrahydrotriquinacen-2-one[8] was transformed into its tetrahydropyranyl ether and the enolate anion of this derivative was condensed with diethyl chlorophosphate.[7b] The resulting enol diethyl phosphate was reduced with lithium in liquid ammonia[7b] and deprotected to give *exo*-2,3-dihydrotriquinacen-2-ol.[7b,10] Following exhaustive catalytic hydrogenation, the saturated exo alcohol was oxidized with the chromium trioxide–pyridine complex in dichloromethane and reduced with lithium aluminum hydride to the endo isomer.[10] Conversion to the mesylate and E_2 elimination on activated alumina delivered the known hydrocarbon,[11] which was brought to analytical purity by preparative VPC as before.

Heats of Hydrogenation. The heats of hydrogenation of triquinacene and its di- and tetrahydro derivatives were measured as follows. By use of a calorimeter for catalytic hydrogenation of alkenes as previously described,[12] aliquot portions of a solution in hexane of triquinacene or of its di- or tetrahydro derivative were injected into the calorimeter in alternation with injections of a thermochemical standard, 1-hexene. The standard molar heat of hydrogenation ($\Delta H_{\mathrm{h,m}} = -30.25$ kcal mol^{-1})[13] permits calculation of $\Delta H_{\mathrm{h,m}}$ of the new compounds from the measured ratio of heats produced within the calorimeter.[12,13] For the current experiments, injections were made by using a GLC syringe with a mechanical stop set at 80 μL. Optimum reproducibility is said to be 0.6% by the manufacturer and was verified before proceeding with these experiments. Reaction times plus instrumental response times were about 10 s. Total run times were 100 s. Gas chromatographic analysis of the calorimeter fluid after nine or more hydrogenations had been run showed a single clean product peak at long retention times. Analysis of samples of calorimeter fluid intentionally contaminated with triquinacene showed a split peak with the satellite at a shorter retention time than the product peak. We estimate that 1% of unreacted triquinacene could have been detected in the calorimeter fluid, had it been present.

Thus, we see that triquinacene is unequivocally stabilized by 4.5 kcal mol^{-1} relative to reference species that lack the cyclic array of three π-bonds. The heats of formation of solid and gaseous hexahydrotriquinacene have been reported in the literature,[14] −38.0 (±0.8) and −24.5 (±0.9) kcal mol^{-1}. These experimental results, the numbers we have measured, and the by now standard assumption[12a] that heats of hydrogenation of hydrocarbons in dilute hexane solution are equivalent to those in the gas phase result in heats of formation of gas-phase triquinacene (**1**), dihydrotriquinacene (**2**), and tetrahydrotriquinacene (**3**) of 53.5 (±1.0), 30.5 (±1.0), and 3.0 (±1.0) kcal mol^{-1}.

The provocative findings, just described, make clear that the low-temperature X-ray analyses of triquinacene[15] prove misleading in not reflecting structural features suggestive of enhanced electronic interaction. In this connection, the crystallographic data for C_{16}-hexaquinacene,[16] a substrate believed to be more ideally tailored to homoconjugation,[17] implicate possible repulsive interactions between its three double bonds. Clearly, the thermochemical test must be applied systematically to series of compounds of this type and such investigations are currently in progress. These data will constitute useful conceptual building blocks for more complete thermochemical understanding of spherically shaped polyquinanes and ultimately of dodecahedrane, a consummate example of this class of organic compounds.

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A General Method for the Selective Binding and Activation of One Aldehyde Enantioface: Synthesis and Reactivity of Rhenium Aldehyde Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}RCH{=}O)]^+PF_6^-$

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A general conversion of achiral aldehydes to chiral alcohols of high optical purity would be of immense utility in organic synthesis. Numerous catalytic[2] and stoichiometric[3] reactions have been described that effect such transformations with varying degrees of generality and success. We now report that the easily generated, chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ selectively binds one aldehyde enantioface and that these aldehyde complexes undergo essentially stereospecific nucleophilic attack. Furthermore, the rhenium Lewis acid can be recycled without racemization.

I. Binding. Methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**1**)[4] and $HPF_6{\cdot}Et_2O$ were reacted (CH_2Cl_2, −78 °C) to give the recently reported coördinatively unsaturated *pyramidal* cation $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+PF_6^-$ (**2**).[5] Addition of isobutyraldehyde, benzaldehyde, and phenylacetaldehyde (3 equiv, −78 °C) to **2** gave η^2-aldehyde complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}RCH{=}O)]^+PF_6^-$ (**3a–c**; Scheme I) in 83–73% yields after recrystallization.[6] The uncommon[7] η^2-coordination mode was assigned on the basis of the CO ^{13}C NMR resonance (81–89 ppm) and the absence of an IR $\nu_{C=O}$. Crude and recrystallized **3a–c** were by all criteria diastereomerically pure, *indicating se-*

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