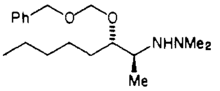
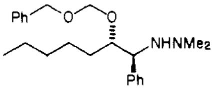
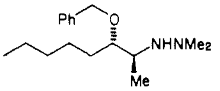
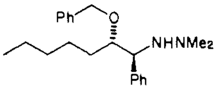
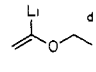
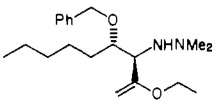
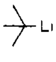
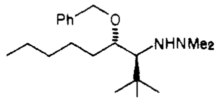
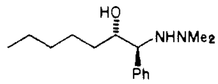
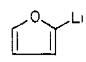
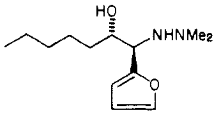
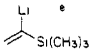
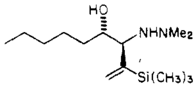
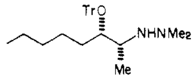
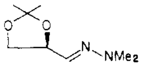
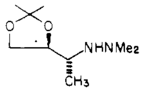
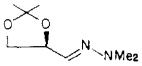
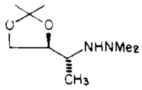
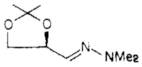
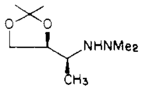
Table I. Reactions of Hydrazones

entry	hydrazone	organometallic reagent[a]	major product[b]	yield, %	threo/erythro[c]
1	1	MeLi		95	97/3
2	1	PhLi		95	>98/2
3	2	MeLi		98	97/3
4	2	PhLi		93	>98/2
5	2	 d		94	>98/2
6	2			98	>98/2
7	3	PhLi		93	>98/2
8	3	 d		85	>98/2
9	3	 e		88	98/2
10	4	MeLi		85	1/10
11		MeLi		95	3/1
12		MeLi[d,f]		75	6/1
13		MeLi[g] (CuI, 0.1 eq)		96	1/3

[a] Reactions were conducted under argon by adding the hydrazone in diethyl ether (0.4 M) to 1.5 equiv of organolithium reagent at -10 °C. The mixture was allowed to warm to 25 °C (over 1 h) and quenched with H_2O. The products were obtained by extractive workup. Entries 7-9 were acidified with 0.1 N HCl and then isolated by extraction after basifying with Na_2CO_3. [b] Entries 1-10 are racemic. [c] Determined by ^1H NMR and/or HPLC. [d] 5 equiv of lithium reagent. [e] 2.5 equiv of lithium reagent. [f] At -55 °C for 5 days, quenched with MeOH at -78 °C. [g] At -20 °C for 3 h, quenched with MeOH at -50 °C, then extracted from saturated aqueous NH_4Cl.

in an enantioselective synthesis of (-)-norpseudoephedine[26] (**7**) (Scheme II). (*S*)-Alcohol **6**[27] was converted to **7** without significant racemization and requiring no chromatography (isolated as the hydrochloride in 92% ee ($[\alpha]_D$ -38.9° (H_2O, *c* 1.0)). The erythro diastereomer was undetectable in the crude ^1H NMR (300 MHz). The conditions (PtO_2, 0.8 equiv/1% HOAc in MeOH (20 mL/mmol)/55 psig of H_2/3.5 h) for clean reductive cleavage of the hydrazine were critical.[28]

Supplementary Material Available: Reaction scheme and optical rotation data for β-adrenergic blocker intermediates; NMR, NOE, IR, and TLC data for compounds **1**-**7** and the products, intermediates, and oxazolidinone derivatives contained in Table I; and X-ray data containing tables of atomic positional and thermal parameters, bond distances, and bond angles for the oxazolidinone derivative of entry 8 of Table I (13 pages). Ordering information is given on any current masthead page.

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(26) For a recent synthesis, see ref 4b.

(27) The *R* isomer of **6** has been reported $[\alpha]_D$ +8.2° (*c* 5.2, benzene): Duveen, D. I.; Kenyon, J. *J. Chem. Soc.* **1939**, 1697-1701. The *S* isomer was prepared in 31% yield [95% ee, $[\alpha]_D$ -7.8° (*c* 5.0, benzene)] by kinetic resolution,[30] using (+)-DIPT.

(28) Various activities of Raney nickel as an hydrogenolysis catalyst resulted in epimerization giving a mixture of norephedrine and norpseudoephedrine.

(29) X-ray structure determinations were kindly provided by J. P. Springer and J. Hirshfield; see supplementary material for the data of entry 8 of Table I.

(30) Hanson, R. M.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922-1925.

Electrochemistry of Quadruply Bonded Molybdenum Dimers. Evidence for Metal-to-Halide Back-Bonding

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Studies of the spectroscopic and photophysical properties of quadruply bonded metal dimers have provided valuable insights about the nature of the metal-metal bonding in the lowest electronic states.[1-3] Results for the redox-active $Mo_2X_4(PR_3)_4$ (X = Cl, Br, I; R = Me, Et, *n*-Pr, *n*-Bu) series[3,4] have been particularly useful, because they have revealed the effects of ligand variations on these electronic energy levels.

This report is concerned with the electrochemical behavior of the $Mo_2X_4(PR_3)_4$ complexes (Table I). The orbital involved in oxidation is δ, while reduction of the neutral complex places an electron in δ*. Except as noted, all redox couples are quasi-reversible in tetrahydrofuran (THF) and methylene chloride solutions at a scan rate of 500 mV/s.[5] Surprisingly, the $Mo_2X_4(PMe_3)_4$ complexes are more easily oxidized and difficult to reduce in the order Cl > Br > I. This is the inverse of the order expected from simple electronegativity arguments, since Cl is more electron withdrawing than Br or I.

It is not likely that this unusual redox behavior is attributable to differences in solvation, since the "inverse halide order" (IHO) also is found for complexes [e.g., $Mo_2X_4(PEt_3)_4$] where the influence of the halide on solubility is small compared to the phosphine. In addition, the same ordering of oxidation potentials[6]

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(1) (a) Trogler, W. C.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 232. (b) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

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(3) (a) Hopkins, M. D.; Gray, H. B. *J. Am. Chem Soc.* **1984**, *106*, 2468. (b) Zietlow, T. C.; Hopkins, M. D.; Gray, H. B. *J. Solid State Chem.* **1985**, *57*, 112.

(4) (a) Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947. (b) Schrock, R. R.; Sturgeoff, L. G.; Sharp, P. R. *Inorg. Chem.* **1983**, *22*, 2801. (c) Ouyang, J.; Zietlow, T. C.; Hopkins, M. D.; Fan, F.-R. F.; Gray, H. B.; Bard, A. J. *J. Phys. Chem.* **1986**, *90*, 3841.

(5) Our criterion for reversibility is that $i_{p,c}/i_{p,a} \simeq 1$. In our experiments the peak-to-peak splittings were greater than 60 mV due to uncompensated solution resistance.[4c]

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.

Acknowledgment. We thank C.-W. Lee for help with some of the measurements. This work was supported by National Science Foundation Grant CHE84-19828. T.C.Z. and M.D.H. gratefully acknowledge Sun Co. graduate fellowships.

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

(7) Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040.

(8) Hopkins, M. D.; Schaefer, W. P.; Bronikowski, M. J.; Woodruff, W. H.; Miskowski, V. M.; Dallinger, R. F.; Gray, H. B. *J. Am. Chem. Soc.*, in press.

(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.

(11) Hurst, R. W.; Heineman, W. R.; Deutsch, E. *Inorg Chem.* **1981**, *20*, 3298.

(12) Brant, P.; Salmon, D. J.; Walton, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 4424.

Is Triquinacene Homoaromatic? A Thermochemical Answer in the Affirmative

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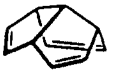
Aromaticity is a well-documented and multifaceted concept in organic chemistry. This is true for neutral and charged carbocycles alike. Homoaromaticity in ions is likewise documented, while in neutral species homoaromaticity has proven a great deal more elusive.[2] Numerous well-designed neutral species 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.


1


2


3

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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(1) (a) University of Maryland. (b) The Ohio State University. (c) Long Island University.

(2) (a) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106. (b) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797.

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(5) Allinger, N. L.; Dodziuk, H.; Rogers, D. W.; Naik, S. N. *Tetrahedron* **1982**, *38*, 1593.

(6) (a) Paquette, L. A.; Kearney, F. R.; Drake, A. F.; Mason, S. F. *J. Am. Chem. Soc.* **1981**, *103*, 5064. (b) Bischof, P.; Bosse, D.; Gleiter, R.; Kukla, M. J.; de Meijere, A.; Paquette, L. A. *Chem. Ber.* **1975**, *108*, 1218.

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