

distance implies that if a metal-metal interaction exists, it is at best a very weak one. Similar weak metal-metal interactions have been recently observed in the related complexes $(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{ZrCp}_2^{23}$ (3) and $(\text{CO})_4\text{Mo}(\mu\text{-PEt}_2)_2\text{HfCp}_2^{24}$ (4). The M-M' distances in 3 and 4 are 3.289 (1) and 3.400 (1) Å, respectively. The difference between the M-M' distances in 2 and 3 is only 0.010 Å, reflecting the similarity of the covalent radii of W and Mo. Although the covalent radii of Zr and Hf are also similar, a longer M-M' distance is observed in 4. This must result from the replacement of the bulky PPh₂ bridges with the sterically less demanding PEt₂ moieties. This substitution results in an increase of the M-P-M' angle from 79.1 (1) to 83.01 (3)°, thus giving rise to the longer M-M' distance.

The synthetic method described above and confirmed by the crystallographic data employs 1 as a "metallo-ligand", providing a convenient method for the incorporation of a group 4³³ metal in a heterobimetallic complex. Current research is directed at the chemistry of related bimetallic species in which Zr and one atom of Pt, Ni, Rh, or Ir have been incorporated. The results of these studies will be reported in due course.²⁵

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Registry No. 1, 86013-25-4; 2, 96807-99-7; *cis*-Mo(CO)₄(NHC₅H₁₀)₂, 65337-26-0.

Supplementary Material Available: Tables S-I-S-IV listing temperature factors, hydrogen atom parameters, angles and distances associated with the phenyl and cyclopentadienyl rings, and observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

(33) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 10, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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¹³C NMR Spectroscopy as a Probe for the Exclusively Steric Effects of Ligand Superstructure on the Binding Constants of Lacunar Macrocyclic Complexes with Dioxygen

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and Daryle H. Busch*

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A variety of transition-metal complexes have been shown to form reversible 1:1 adducts with molecular oxygen.¹⁻⁷ For structurally similar complexes, the formation of the metal-dioxygen complex is generally thought to depend on two factors:

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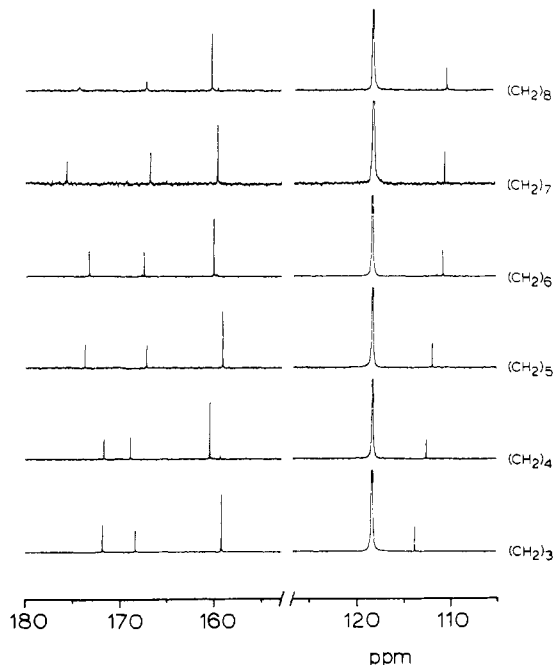


Figure 1. ¹³C NMR spectra for the complexes $[\text{Ni}\{\text{Me}_2(\text{MeN})_2(\text{CH}_2)_n[16]\text{cyclidene}\}(\text{PF}_6)_2]$ in acetonitrile-*d*₃.

Table I. Carbon-13 Chemical Shift Data for the Complexes $[\text{Ni}\{\text{Me}_2(\text{MeN})_2(\text{CH}_2)_n[16]\text{cyclidene}\}(\text{PF}_6)_2]$ in Acetonitrile-*d*₃

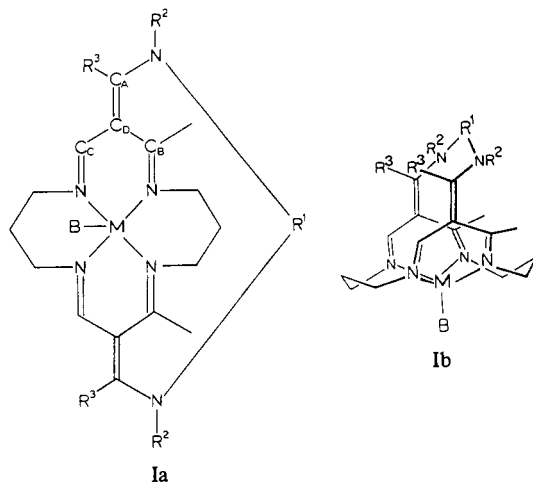
n	δ ^a			
	A ^b	B ^b	C ^b	D ^b
3	171.85	168.36	159.29	113.79
4	171.72	168.93	160.51	112.60
5	173.73	167.22	159.15	112.00
6	173.32	167.54	160.14	110.91
7	175.74	166.90	159.75	110.71
8	174.41	167.29	160.33	110.46

^aData were obtained at 302 K; error is ±0.01 ppm. ^bFor the location of carbons A, B, C, and D, see structure Ia.

(1) the electron density at the metal and (2) the size and shape of the binding site as determined by the ligand superstructure.² In certain cases it is possible to separate the contributions of the electronic and steric factors by relating the equilibrium constant for dioxygen formation (*K*_{O₂}) to some physically measurable parameter of the complex. For example, Basolo was able to show that a linear relationship exists between log *K*_{O₂} and the Co^{II} to Co^{III} half-wave potential (*E*_{1/2}) for a series of Schiff base complexes.⁸ In order to account for this correlation, *E*_{1/2} was taken as a direct measure of the electron density on Co^{II}. Short of a series of crystal structures (which in no way guarantees an accurate reflection of solution chemistry), the task of quantifying the steric protection offered by ligand superstructure via some conveniently measured physical parameter is considerably more difficult to achieve.

Over the past several years, we have reported on the reversible binding of dioxygen to Co^{II} and Fe^{II} complexes based on the lacunar macrocycles that we have termed cyclidenes (structure I).^{9,10} A unique feature of this macrocycle is the persistent void that allows coordination of dioxygen while protecting the bound O₂ from certain other reactions. For the series of complexes $[\text{Co}\{\text{Me}_2(\text{MeN})_2(\text{CH}_2)_n[16]\text{cyclidene}\}]^{2+}$ (structure I, where M

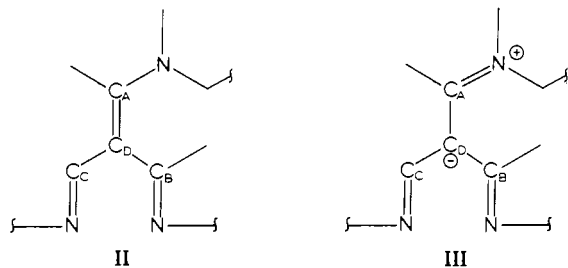
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- (10) (a) Herron, N.; Zimmer, L. L.; Grzybowski, J. J.; Olszanski, D. J.; Jackels, S. C.; Callahan, R. W.; Cameron, J. H.; Christoph, G. G.; Busch, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 6585-6596. (b) Herron, N.; Cameron, J. H.; Neer, G. L.; Busch, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 298-301.



= Co, $R^3 = \text{Me}$, $R^2 = \text{Me}$, $R^1 = (\text{CH}_2)_3$ to $(\text{CH}_2)_8$, and B is some axial base), we have found ^{13}C NMR spectroscopy of the analogous Ni complexes to be a useful technique for quantifying the steric restriction offered by the polymethylene bridge.

The ^{13}C NMR spectra and chemical shift data for selected carbons in the Ni-cyclidene complexes with polymethylene bridges are given in Figure 1 and Table I, respectively. These carbons are denoted as C_A , C_B , C_C , and C_D as indicated in structure Ia. The instrument used to acquire the carbon-13 data was a Bruker AM500 NMR spectrometer operating at 125.76 MHz. The spectra were obtained in acetonitrile- d_3 at 302 K by using a Waltz 16 decoupling program at 1 W, with a sweep width of 25 000 Hz acquired over 32K data points. A value of 1.30 ppm was assigned to the peak attributed to the CD_3 group of the CD_3CN solvent and maintained throughout the experiment.

For carbons A, B, and C the chemical shifts increase and decrease as the polymethylene bridge cycles between even and odd numbers of carbons (see Figure 1). Although this cycling may be apparent in the chemical shift of carbon D (δ_D), it is small compared to the steady decrease in chemical shift with increasing bridge length. The relationship between δ_D and bridge length is shown graphically in Figure 2. The progressive decrease in δ_D with increasing bridge length results, at least in part, from a twisting strain in the $C_A\text{-N}$ bond afforded by the polymethylene bridge, as illustrated by resonance structures II and III. When



the bridge length is decreased and hence the twisting strain in the $C_A\text{-N}$ bond is increased, the contribution from resonance structure III becomes less important. The result is a decrease in the electron density on carbon D, and δ_D is shifted downfield. Although profoundly affecting the chemical shift of carbon D, the interaction is a subtle one and little or no effect is transmitted onto the electron density at the metal center, as seen by examining the electrochemical data in Table II.

The $E_{1/2}$ values given in Table II correspond to the $\text{Ni}^{\text{III/II}}$ reversible couple. Clearly the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ oxidation potential is relatively insensitive to the length of the polymethylene bridge, suggesting that the variation in bridge length must not be greatly affecting the electron density at the metal. Therefore, since $E_{1/2}$ is insensitive to bridge length, it would seem that the chemical shift of carbon D is measuring some aspect of the tension in the polymethylene bridge, which has little effect on the electron density at the metal. This in turn should reflect the bridge length and ultimately the steric restriction about the persistent void in these

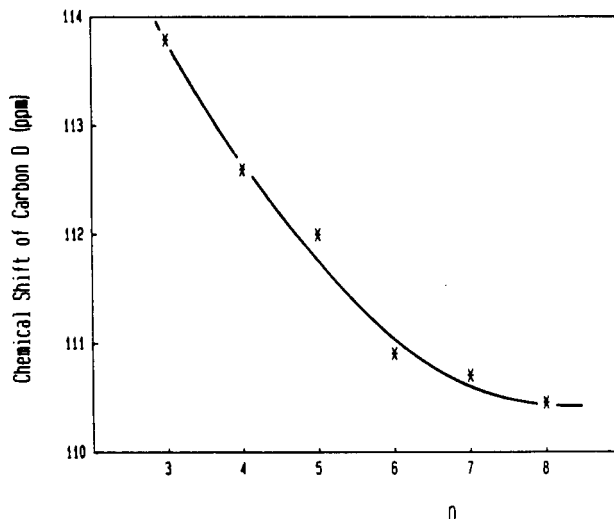


Figure 2. Graph of chemical shift vs. the number of methylene units in the bridge (n) for carbon D in the complexes $[\text{Ni}\{\text{Me}_2(\text{MeN})_2(\text{CH}_2)_n\text{-[16]cyclidene}\}](\text{PF}_6)_2$ in acetonitrile- d_3 . (See Structure Ia for the location of carbon D.)

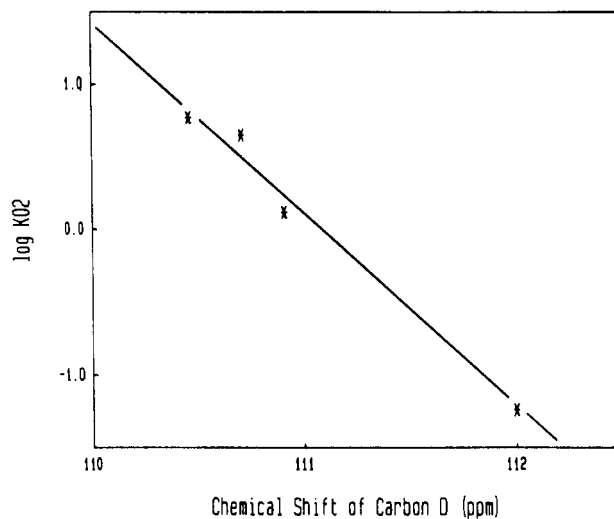


Figure 3. Graph of $\log K_{O_2}$ for the complexes $[\text{Co}\{\text{Me}_2(\text{MeN})_2(\text{CH}_2)_n\text{-[16]cyclidene}\}](\text{PF}_6)_2$ in 1.5 M 1-methylimidazole/acetonitrile at 0 °C vs. the chemical shift of carbon D for the Ni analogue in acetonitrile- d_3 .

Table II. Half-Wave Potentials^{a,b} for the Complexes $[\text{Ni}\{\text{Me}_2(\text{MeN})_2(\text{CH}_2)_n\text{-[16]cyclidene}\}](\text{PF}_6)_2$ in Acetonitrile

n	$E_{1/2}$, V	n	$E_{1/2}$, V
3	0.79	6	0.76
4	0.79	7	0.78
5	0.78	8	0.77

^aHalf-wave potentials were measured by using a rotating platinum disk electrode (1800 rpm) vs. $\text{Ag}/0.1 \text{ M AgNO}_3$ in CH_3CN with 0.1 M tetrabutylammonium fluoroborate as the supporting electrolyte.

^bThese potentials have been reported previously; however, they have been verified (and in some cases corrected) in ref 12.

lacunar complexes^{9,10b} (note structure Ib). We chose to explore this relationship by examining the correlation between the chemical shift of carbon D and K_{O_2} for the analogous cobalt complexes. The results of this analysis are illustrated in Figure 3.

The dioxygen binding constants for the cobalt complexes were measured in 1.5 M 1-methylimidazole/acetonitrile at 0 °C. The experimental details have appeared elsewhere.^{10a} The use of 1-methylimidazole as an axial base and 0 °C temperatures are necessary in order to increase K_{O_2} to within a reliably measurable range; however, even under these conditions, K_{O_2} values for the C_3 and C_4 complexes are too small to be measured. In Figure 3, a plot of $\log K_{O_2}$ vs. δ_D for the $C_5\text{-}C_8$ -bridged complexes shows

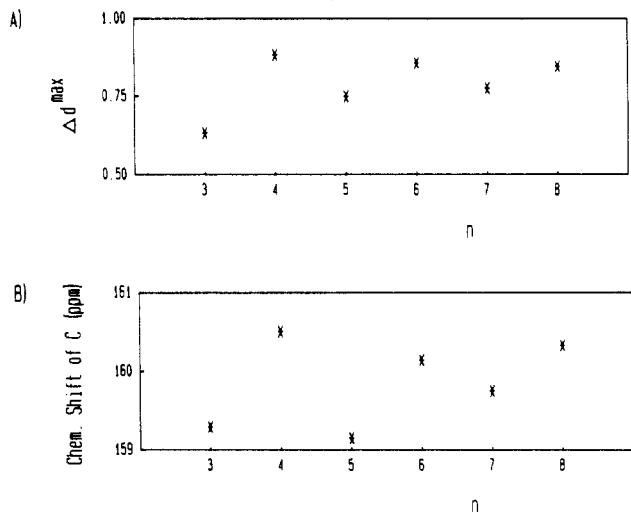


Figure 4. (a) Graph of the *difference* in the maximum terminal carbon to terminal carbon chain length between $(\text{CH}_2)_n$ and $(\text{CH}_2)_{n-1}$, Δd^{max} , vs. n assuming an arbitrary C–C bond length of 1 and a tetrahedral angle of 109.5° . (b) Graph of chemical shift vs. n for the complexes $[\text{Ni}\{\text{Me}_2(\text{MeN})_2(\text{CH}_2)_n[16]\text{cyclidene}\}(\text{PF}_6)_2]$ in acetonitrile- d_3 .

that a linear relationship exists with $r = -0.99$.

The linear correlation is surprisingly good considering the qualitative nature of the parameter employed for bridge length, i.e. the number of methylene units. In fact, assuming a constant C–C bond length and a tetrahedral angle of 109.5° , one can show that the increase in the maximum terminal carbon to terminal carbon distance for a polymethylene chain will follow an odd/even

cycle not unlike that observed for the chemical shift data of carbons A, B, and C. A graph of the *difference* in maximum chain lengths between $(\text{CH}_2)_n$ and $(\text{CH}_2)_{n-1}$ vs. n is shown in Figure 4a. A graph of the chemical shift for carbon C vs. n in Figure 4b shows the similarity in the odd/even cycle. Note that the amplitude of the cyclic change decreases as chain length increases. As the polymethylene bridges become longer and less rigid, the effect of changing the bridge length by one methylene unit should become less important in terms of imposing a twisting strain. It follows that the changes in chemical shift should also decrease, as supported by the chemical shift data for carbon D (see Figure 2).

Although a *strict* linear relationship may be fortuitous for the $\text{C}_5\text{--C}_8$ -bridged complexes, the general trend of increasing K_{O_2} with increasing bridge length has been noted.^{9,10a,11} This series of polymethylene-bridged complexes serves to point out the potential utility of NMR spectroscopy in measuring the steric restrictions offered by ligand superstructure.

Finally, it should be noted that in coordinating solvents such as acetonitrile, $E_{1/2}$ for the cobalt polymethylene-bridged complexes does show a dependence on bridge length; however, this does not reflect a change in electron density at the cobalt center. Instead, the relationship between $E_{1/2}$ and bridge length is complicated and has been explained in terms of a change in coordination number upon oxidation of Co^{II} to Co^{III} .¹²

Acknowledgment. Support of the National Science Foundation is gratefully acknowledged.

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Additions and Corrections

1985, Volume 24

Magdalena J. van der Merwe, Jan C. A. Boeyens,* and Robert D. Hancock*: Crystallographic and Thermodynamic Study of Metal Ion Size Selectivity in the Ligand 1,4,7-Triazacyclononane- N,N' - N'' -triacetate.

Page 1209. Table II (crystal data) was scrambled accidentally with another file. Corrected or deleted information follows:

	$\text{H}_3\text{O}[\text{Ni}(\text{TACNTA})]$	$\text{CuCl}[\text{TACNTAH}_2]$
formula	$\text{C}_{12}\text{H}_{21}\text{N}_3\text{O}_7\text{Ni}$	$\text{C}_{12}\text{H}_{20}\text{N}_3\text{O}_6\text{ClCu}$
M_r	378.04	401.31
space group	$P3c1$	$P2_12_12_1$
a , Å	8.529 (6)	13.405 (7)
b , Å		11.151 (6)
c , Å	12.757 (7)	10.400 (6)
V , Å ³	803.67	1554.58
$\mu(\text{Mo K}\alpha)$, cm^{-1}	12.47	15.33
Z	2	4
D_c , g cm^{-3}	1.56	1.71
$F(000)$	396	828
scan range (θ), deg	2–23	2–23

All cell angles are fixed by symmetry. The fractional atomic coordinates (x , y , z ; $\times 10^4$), with esd's, of the Cu and Cl atoms in the structure of the copper compound are as follows:

Cu	2002 (1)	1421 (1)	–1846 (1)
Cl	842 (2)	149 (3)	9036 (3)

—Jan C. A. Boeyens