National Science Foundation, Grant No. INT-8304329, for additional support.

Registry No. $Ru(H_2O)_2(THF)_2(tos)_2$, 96826-78-7; $[Ru(H_2O)_6](tos)_2$, 15694-44-7; $Ru(H_2O)_2(PPh_3)_2(tos)_2$, 96826-79-8; $Ru(dppe)_2(tos)_2$, 96826-80-1; *cis*-$RuH_2(dppe)_2$, 41753-60-0; $Ru(PPh_3)(C_6H_6)(tos)_2$, 96826-81-2; $[Ru(H_2O)_3(C_6H_6)](tos)_2$, 96826-82-3; $RuH_2(PPh_3)(C_6H_6)$, 96826-83-4.

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Heterobimetallic Complexes. 2.[1] Preparation and Crystal and Molecular Structure of $(C_5H_5)_2Zr(\mu\text{-}P(C_6H_5)_2)_2Mo(CO)_4$

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Heterobinuclear transition-metal complexes have been the subject of numerous recent studies.[1-25] The interest in such species stems from both the relevance of bimetallic compounds to bioinorganic systems[3,4] and the potential for applications in catalysis.[5-25] Of particular interest is the incorporation of both early and late transition metals into the same complex.[1,21-25] Such compounds are expected to exhibit the ability to activate and polarize substrates like CO.

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement for $(C_5H_5)_2Zr(\mu\text{-}P(C_6H_5)_2)_2Mo(CO)_4$

formula	$MoZrP_2O_4C_{38}H_{30}$
cryst color, form	yellow, blocks
a, Å	18.418 (2)
b, Å	18.435 (3)
c, Å	10.082 (1)
cryst system	orthorhombic
space group	$P2_12_12_1$
vol, $Å^3$	3423 (1)
d_{calcd}, g/cm^3	1.55
Z	4
cryst faces	(001), (001), (100), (010), (010)
cryst dimens, mm	0.27 × 0.31 × 0.73
abs coeff μ, cm^{-1}	7.12
radiation (λ, Å)	Mo Kα (0.71069)
temp, °C	24
scan speed, deg/min	2.0–5.0 ($\theta/2\theta$ scan)
scan range, deg	1.0 below Kα_1 to 1.0 above Kα_2
bkgd/scan time ratio	0.5
data collcd	3285: 20 of 4.5° to 50 (+*h*,+*k*,+*l*)
no. of unique data ($F_o^2 > 3\sigma(F_o^2)$)	2961
no. of variables	415 (2 blocks)
R	2.34
R_w	2.62

Our research is aimed at the development of synthetic methods for the incorporation of early transition elements into heterobimetallic complexes. To this end we are exploring the chemistry of early-transition-metal "metalloligands", that is complexes that are early-transition-metal species and yet have the capability of acting as ligands for other metals. We have recently reported the synthesis of the titanium species $(C_5H_5)_2Ti(SCH_2CH_2P(C_6H_5)_2)_2$,[1] which is capable of acting as a "metalloligand" for complexation of Cu(I). In this paper we describe the use of the complex $(C_5H_5)_2Zr(P(C_6H_5)_2)_2$ (**1**) as a "metalloligand". The preparation, the characterization, and the results of an X-ray crystallographic investigation of the $Mo(CO)_4$ complex of **1** are presented herein. The implications of these results are discussed below.

Experimental Section

All preparations were done under an atmosphere of dry, O_2-free, N_2. Solvents were reagent grade and were distilled from the appropriate drying agents N_2 and degassed by the freeze–thaw method at least three times prior to use. ^1H NMR spectra were recorded on Bruker CXP-80 and CXP-100 spectrometers using $Si(CH_3)_4$ as the reference. ^{31}P NMR spectra were recorded on a Bruker CXP-100 spectrometer operating at 36.44 MHz with broad band proton decoupling. Samples were sealed in 5-mm tubes under a N_2 atmosphere. The ^{31}P chemical shifts are reported relative to 85% H_3PO_4. Infrared data were recorded on a Beckman IR-12 spectrometer. Melting points were recorded on a Fisher melting point apparatus and were not corrected. UV–vis spectra were recorded on a Shumadzu 240 spectrometer. Combustion analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada. $(C_5H_5)_2ZrCl_2$ and $Mo(CO)_6$ were purchased from Aldrich Chemical Co. $(C_6H_5)_2PH$ was purchased from Strem Chemical Co. *cis*-$Mo(CO)_4(NHC_5H_{10})_2$ was prepared by literature methods.[26]

Preparation of $(C_5H_5)_2Zr(P(C_6H_5)_2)_2$ (1). Initially we employed the method of Baker et al.[27] to prepare **1**. This required the reaction of $(C_5H_5)_2ZrCl_2$ with 2 equiv of $LiP(C_6H_5)_2$ at −80 °C in THF. Wade and co-workers[28] recently reported the preparation of **1** at room temperature. In subsequent preparations of **1** this method was used. **1** was found to be an extremely air-sensitive and reactive compound; thus all isolation procedures and subsequent manipulations were performed in an inert-atmosphere glovebox (N_2 atmosphere).

Preparation of $(C_5H_5)_2Zr(\mu\text{-}P(C_6H_5)_2)_2Mo(CO)_4$ (2). *cis*-$Mo(CO)_4(NHC_5H_{10})_2$ (0.34 g, 0.90 mmol) dissolved in benzene was slowly added to a benzene solution of $(C_5H_5)_2Zr(P(C_6H_5)_2)_2$ (0.513 g, 0.87 mmol). The solution changed from a dark purple to a very clear orange-yellow upon stirring for 1 h. The volume was slowly reduced, and

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Table II. Positional Parameters[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Mo	3355 (1)	855 (1)	1251 (1)	C24	1569 (3)	3426 (3)	3679 (5)
Zr	4621 (1)	2121 (1)	1251 (1)	C25	1464 (3)	2711 (3)	3365 (5)
F1	3205 (1)	2220 (1)	970 (1)	C26	1956 (2)	2342 (3)	2610 (5)
P2	4719 (1)	706 (1)	1531 (1)	C31	5090 (2)	325 (2)	3067 (4)
C1	5326 (3)	2926 (3)	−254 (6)	C32	4661 (3)	130 (3)	4134 (4)
C2	5648 (3)	2235 (3)	−334 (6)	C33	4964 (3)	−107 (3)	5332 (6)
C3	5148 (3)	1776 (3)	−982 (5)	C34	5711 (3)	−175 (3)	5448 (5)
C4	4525 (2)	2176 (3)	−1266 (5)	C35	6135 (3)	−7 (3)	4370 (5)
C5	4631 (3)	2884 (3)	−805 (5)	C36	5843 (2)	238 (3)	3222 (5)
C6	4730 (3)	3153 (3)	2839 (5)	C41	5179 (2)	86 (2)	355 (4)
C7	4272 (3)	2651 (3)	3476 (5)	C42	5895 (2)	198 (3)	11 (5)
C8	4681 (3)	2127 (3)	3743 (5)	C43	6263 (3)	−326 (4)	−785 (5)
C9	5391 (3)	2137 (3)	3285 (5)	C44	5931 (3)	−933 (3)	−1205 (5)
C10	5426 (3)	2829 (3)	2763 (6)	C45	5217 (3)	−1036 (3)	−885 (5)
C11	2818 (2)	2589 (2)	−582 (4)	C46	4838 (3)	−538 (2)	−118 (5)
C12	2736 (3)	3334 (2)	−737 (5)	C51	3129 (3)	1056 (3)	3190 (5)
C13	2495 (3)	3640 (3)	−1907 (5)	C52	2303 (3)	804 (3)	806 (5)
C14	2322 (3)	3204 (3)	−2937 (5)	C53	3305 (3))	−194 (2)	1706 (5)
C15	2394 (3)	2464 (3)	−2827 (5)	C54	3553 (3)	633 (3)	−712 (5)
C16	2630 (2)	2163 (3)	−1651 (5)	O1	2986 (2)	1153 (3)	4265 (4)
C21	2584 (2)	2681 (2)	2150 (4)	O2	1702 (2)	747 (3)	513 (5)
C22	2695 (3)	3393 (2)	2520 (5)	O3	3244 (3)	−795 (2)	2009 (5)
C23	2191 (3)	3767 (3)	3267 (5)	O4	3651 (3)	481 (2)	−1778 (4)

[a] Multiplied by 10^4.

Table III. Selected Bond Distances and Angles

		Distances (Å)			
Mo–Zr	3.299 (1)	Zr–C1	2.489 (6)	Mo–C51	2.033 (5)
Mo–P1	2.547 (1)	Zr–C2	2.484 (5)	Mo–C52	1.991 (5)
Mo–P2	2.543 (1)	Zr–C3	2.532 (5)	Mo–C53	1.990 (5)
Zr–P1	2.631 (1)	Zr–C4	2.546 (5)	Mo–C54	2.054 (5)
Zr–P2	2.630 (1)	Zr–C5	2.505 (5)	C51–O1	1.129 (6)
P1–C11	1.849 (4)	Zr–C6	2.496 (5)	C52–O2	1.149 (6)
P1–C21	1.856 (4)	Zr–C7	2.530 (5)	C53–O3	1.155 (6)
P2–C31	1.832 (4)	Zr–C8	2.521 (5)	C54–O4	1.125 (6)
P2–C41	1.851 (4)	Zr–C9	2.494 (5)		
		Zr–C10	2.496 (6)		
		Angles (deg)			
P1–Mo–P2	103.1 (1)	Mo–P1–C21	116.6 (1)	P1–Mo–C51	84.6 (1)
Mo–P1–Zr	79.1 (1)	Mo–P1–C11	120.0 (1)	P1–Mo–C52	85.2 (1)
P1–Zr–P2	98.5 (1)	Zr–P1–C21	125.0 (1)	P1–Mo–C53	168.8 (1)
Zr–P2–Mo	79.2 (1)	Zr–P1–C11	119.9 (1)	P1–Mo–C54	96.2 (1)
Mo–C51–O1	177.9 (4)	Mo–P2–C31	120.2 (1)	P2–Mo–C51	96.6 (1)
Mo–C52–O2	176.8 (4)	Mo–P2–C41	116.6 (1)	P2–Mo–C52	168.9 (1)
Mo–C53–O3	176.4 (4)	Zr–P1–C31	129.8 (1)	P2–Mo–C53	85.1 (1)
Mo–C54–O4	176.8 (4)	Zr–P1–C41	125.0 (1)	P2–Mo–C54	84.8 (1)
C51–Mo–C53	86.9 (2)	C31–P2–C41	97.8 (2)		
C51–Mo–C52	91.5 (2)	C11–P1–C21	97.8 (2)		
C54–Mo–C53	92.1 (2)	CP1–Zr–CP2	127.0 (5)		
C54–Mo–C52	87.0 (2)				
C52–Mo–C53	87.8 (2)				
C51–Mo–C54	178.2 (2)				

filtration led to the isolation of a fine yellow powder, 0.56 g (80%). Anal. Calcd for $C_{38}H_{30}O_4P_2ZrMo$: C, 57.07; H, 3.78. Found: C, 57.68; H, 4.22. IR: 2010, 1930, 1895 cm^{-1}. ^1H NMR: δ 7.4 (m, 20 H), 5.20 (s, 10 H). $^{31}P\{^1H\}$ NMR: δ 175.5 (s). UV–vis: λ (ϵ) 306 nm (6220 M^{-1} cm^{-1}, 347 nm (1980 M^{-1} cm^{-1}), 416 nm (910 M^{-1} cm^{-1}).

X-ray Data Collection and Reduction. Crystallization was performed by the slow diffusion of diethyl ether into a solution of THF (25 mL) containing 100 mg of **2**. Since solutions of **2** were found to be very air sensitive, the elongated yellow blocks were mounted in capillaries under an atmosphere of N_2 in a glovebox. Diffraction experiments were performed on a four-circle Syntex $P2_1$ diffractometer with graphite-monochromatized Mo Kα radiation. The initial orientation matrix was obtained from 15 machine-centered reflections selected from a rotation photograph. These data were used to determine the crystal system. Partial rotation photographs around each axis were consistent with an orthorhombic crystal system. Ultimately, 27 high-angle reflections (17° < 2θ < 40°) were used to obtain the final lattice parameters and the orientation matrix. Machine parameters, Crystal data, and data collection parameters are summarized in Table I. The observed extinctions were consistent only with the space group $P2_12_12_1$. $+h,+k,+l$ data were collected in two shells (4.5 ° < 2θ < 45.0° and 45.0° < 2θ < 50.0°). Three standard reflections were recorded every 97 reflections; their intensities showed no statistically significant change over the duration of data collection. No absorption correction was applied to the data (μ = 7.12 cm^{-1}). The data were processed by using the SHELX-76 program package on the computing facilities at the University of Windsor. A total of 2961 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the tabulation of Cromer and Waber.[29,30] The Mo and Zr atom positions were determined by the heavy-atom (Patterson) method. The remaining non-hydrogen atoms wre located from successive difference Fourier map calculations. Refinement was carried out by using full-matrix least-squares techniques on F, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of least-squares refinement, all non-hydrogen

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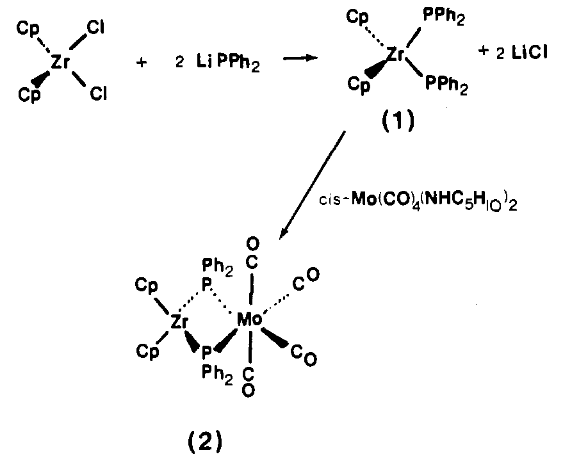
Scheme I



atoms were assigned anisotropic temperature factors. The hydrogen atom contributions were included, C–H bond lengths of 0.95 Å were assumed, and hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the bonded carbon atom. This gave $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.0234$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.0262$. The maximum Δ/σ on any of the parameters in the final cycles was 0.002. A final difference Fourier map calculation showed no peaks of chemical significance; the largest peak was 0.4 e and was associated with one of the C_5H_5 groups. The following data are tabulated: positional parameters (Table II); interatomic distances and angles (Table III). Temperature factors (Table S-I), hydrogen atom parameters (Table S-II), angles and distances associated with the phenyl and cyclopentadienyl rings (Table S-III), and values of $10|F_o|$ and $10|F_c|$ (Table S-IV) have been deposited as supplementary material.

Results and Discussion

The reaction of $LiPPh_2$ with $(C_5H_5)_2ZrCl_2$ to produce the species **1** has been recently described by two groups.[27,28] We have employed modified versions of both routes to prepare this complex. Both methods give good yields of the very air-sensitive zirconium diphosphide species; however, the procedure of Wade et al.[28] was found to be a technically more convenient synthesis. Reaction of **1** with $Mo(CO)_4(NHC_5H_{10})_2$ was performed under strictly anaerobic conditions in benzene solution. Gradually, after the two reactants were mixed, the color of the solution faded from dark purple to a translucent orange-yellow. The dramatic color change is indicative of disruption of the phosphide–zirconium charge-transfer absorption present in **1**.[27] Concentration and filtration resulted in the isolation of an orange-yellow solid. The IR spectrum of this product is consistent with a disubstituted Mo carbonyl species. The ^1H NMR spectrum shows resonances corresponding to phenyl and cyclopentadienyl protons in the ratio of 2:1. $^{31}P\{^1H\}$ NMR shows only a single line at 175.5 ppm, indicative of chemically equivalent phosphorus atoms. These observations together with the combustion analysis data are consistent with the formulation of this orange-yellow product as **2**. The complete synthetic route is outlined in Scheme I. This synthesis demonstrates the utility of compound **1** as a "metalloligand". Further it suggests that use of **1** may provide a convenient method for the synthesis of compounds containing Zr and other transition-metal elements.[24,25]

Single crystals of **2** were obtained by slow anaerobic diffusion of diethyl ether into a THF solution of **2**. An X-ray crystallographic study of this species revealed that the crystals were made up of unit cells each containing four discreate molecules. The closest nonbonded contact between molecules in the unit cell is 2.586 Å (H9–H14). Selected interatomic distances are given in Table III. An ORTEP drawing of the molecule is shown in Figure 1. The geometry of the Zr is pseudotetrahedral while that of the Mo is pseudooctahedral. Two π-bonded cyclopentadienyl rings and two phosphorus atoms comprise the Zr coordination sphere. The Zr–C bond distances average 2.509 (20) Å. The Zr–P distances are equivalent at 2.631 (1) Å. This is in contrast to the inequivalent Hf–P bond length found in the Hf analogue of **1**.[27] The angle between the vectors from Zr to the centers of the cyclopentadienyl rings is 127.0, while the P–Zr–P angle is 98.5 (1)°. The two phosphorus atoms and four carbonyl groups complete the Mo coordination sphere. The Mo–P distances are typical[24] and average 2.545 (1) Å. The Mo–C distances also fall within expected ranges.[24] The Mo–C bonds trans to phosphorus are shorter than those cis to phosphorus (i.e. 1.990 (5) vs. 2.043 (5) Å). The shorter metal–carbon bonds are associated with a longer C–O bond distance and vice versa. These effects are consistent with simple donor strength and π-back-bonding arguments. The C–Mo–C and P–Mo–C angles reveal a small distortion of the geometry about the Mo. The axial carbonyls are tilted by about 6° with respect to the plane containing the other ligands around the Mo. The cause of this distortion is not clear, but steric interactions of the carbonyls with the phenyl rings on the phosphorus atoms are suspected. Close contact of O4–H16 (2.828 Å) was observed.

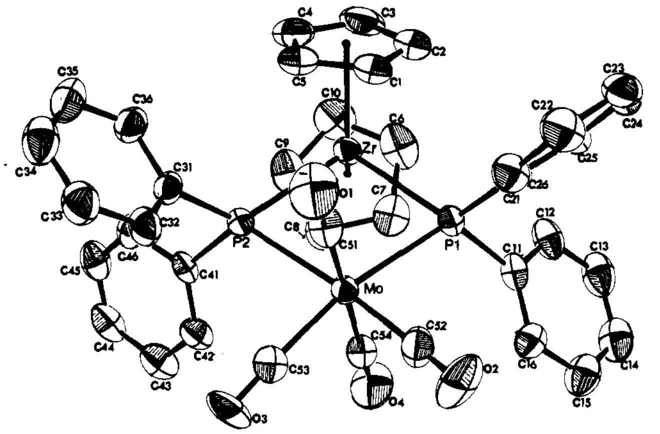


Figure 1. ORTEP drawing of molecule 2. 50% thermal ellipsoids are shown, and hydrogen atoms are omitted for clarity.

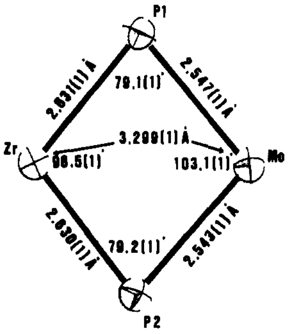


Figure 2. ORTEP drawing of the ZrP_2Mo core.

The upfield shift of the cyclopentadienyl resonances in the ^1H NMR spectrum of **2** suggests an increase in electron density on the zirconium upon complexation with the Mo moiety. Thus a Mo (d^6) to Zr (d^0) interaction similar to the Cu(I) (d^{10}) to Ti(IV) (d^0) dative bond observed in the complex $[(C_5H_5)_2Ti(SCH_2CH_2PPh_2)_2Cu]BF_4$ might be postulated. The crystallographic data show that the four atoms of the core are coplanar. The details of the geometry of the core are illustrated in Figure 2. The angles at phosphorus are constrained to 79.1 (1)° while those at Zr and Mo are 98.5 (1) and 103.1(1)°, respectively. The P–Mo–P angle in **2** is greater than 90° while the P–Zr–P angle is larger than the corresponding angles in the metallocene dihalides.[31] Such distortions of the angles about a four-atom core have been used as criteria for metal–metal interactions in other systems.[32] However, the Mo–Zr distance is 3.299 (1) Å. This is considerably longer than the sum of the covalent radii. Clearly, despite the implications from some of the above data, the Mo–Zr

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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 $(CO)_4W(\mu\text{-}PPh_2)_2ZrCp_2$[23] (**3**) and $(CO)_4Mo(\mu\text{-}PEt_2)_2HfCp_2$[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 PPh_2 bridges with the sterically less demanding PEt_2 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 "metalloligand", providing a convenient method for the incorporation of a group 4[33] 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*-$Mo(CO)_4(NHC_5H_{10})_2$, 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.

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(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 nd 2. The d-transition elements comprise groups 3 through 12, 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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^{13}C NMR Spectroscopy as a Probe for the Exclusively Steric Effects of Ligand Superstructure on the Binding Constants of Lacunar Macrobicyclic Complexes with Dioxygen

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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:

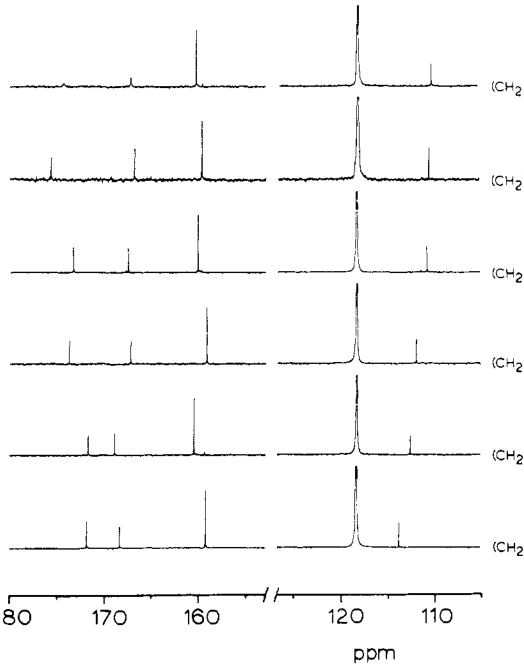

Figure 1. ^{13}C NMR spectra for the complexes $[Ni\{Me_2(MeN)_2(CH_2)_n[16]cyclidene\}](PF_6)_2$ in acetonitrile-d_3.

Table I. Carbon-13 Chemical Shift Data for the Complexes $[Ni\{Me_2(MeN)_2(CH_2)_n[16]cyclidene\}](PF_6)_2$ in Acetonitrile-d_3

	δ^a			
n	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

[a] Data were obtained at 302 K; error is ±0.01 ppm. [b] For 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_{O_2}) to some physically measurable parameter of the complex. For example, Basolo was able to show that a linear relationship exists between log K_{O_2} 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 macrobicycles 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 O_2 from certain other reactions. For the series of complexes $[Co\{Me_2(MeN)_2(CH_2)_n[16]cyclidene\}]^{2+}$ (structure I, where M

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