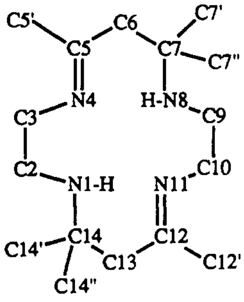

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racemic form, with the two amine (N1 and N8) hydrogens on the same side as the aquo ligand. Thus the two axial macrocycle methyl groups are on the same face as the methyl ligand. This is the so-called secondary isomer of the methyl, aquo complex. The $[CoL(CH_3)(OH_2)](CF_3SO_3)_2$ unit is stabilized by two sets of hydyrogen bonds (Table S6) between two of the oxygen atoms on each triflate anion and the hydrogen atoms of a macrocycle N–H and the axially coordinated water molecule. Analogous hydrogen-bonding interactions were found[9] to be important for the five-coordinate cobalt(II) complexes *prim,rac*-$CoL(OH_2)^{2+}$ and *prim,rac*-$CoL(OClO_3)^+$. These hydrogen-bonding interactions, as well as methyl–methyl repulsion on the secondary face of the macrocycle, cause a folding of the macrocycle toward the axial water ligand and away from the axial methyl ligand. The fold, defined as the angle between the N1, N4, N8, and the N1, N8, N11 planes, is 6.8°.

Some qualitative experiments were carried out in order to compare the reactivity of *sec,rac*-$CoL(CH_3)(OH_2)^{2+}$ with its isomers. In these, evidence was found that SCN^- rapidly[7] replaces the axial water molecule to give a SCN^- adduct with $\lambda_{max} = 450$ and 365 nm in 0.01 M $HClO_4$. No evidence was found for Cl^-, Br^-, or I^- binding ($K \leq 10$ M^{-1}). Treatment of the crude mixture of *sec,rac*-$CoL(CH_3)(OH_2)^{2+}$ (80%) and *meso*-$CoL(CH_3)(OH_2)^{2+}$ with 0.01 M carbonate buffer (pH 10.3 in D_2O, followed by reacidification to pH 1.6, yielded a mixture ca. 20% in the primary *rac* isomer with the secondary, rac isomer remaining unchanged. Given that *meso*-to-primary, *rac* isomerization is known to occur readily[12] and that the primary, *rac* isomer is favored 5:1 over the *meso* isomer at equilibrium,[7] we must conclude that the secondary, *rac*/primary, *rac* equilibrium is slow under these conditions.

Discussion

The structure of the secondary isomer of *rac*-$CoL(CH_3)(OH_2)^{2+}$ may be compared with that determined by Heeg et al. for the primary isomer.[13] The Co–C bond distances are the same (1.980 (8) vs 1.971 (6) Å), but the Co–OH_2 distance is 0.025 (5) Å shorter in the secondary (2.090 (5) Å) than in the primary (2.115 (4) Å) isomer. There are no significant differences between the two isomers in the intramacrocycle bond distances. However, the macrocycle folding described above for the secondary isomer is responsible for differences in the bond angles. (The fold angle is only 3.1° in the primary isomer.) The largest difference is seen in the N_{am}–Co–N_{am} angle, which is 179.0 (3)° in the primary isomer and 171.6 (3)° in the secondary isomer. The cobalt atom lies 0.087 Å out of the plane of the four nitrogen atoms toward the axial methyl ligand in the secondary isomer compared with 0.009 Å in the primary isomer, and the axial methyl groups are more swept back in the former due to the larger volume of the axially coordinated methyl ligand.

As was mentioned previously,[9] the most remarkable aspect of this study is the fact that reaction of *rac*-CoL^{2+} with methyl radicals results in Co–C bond formation at the sterically hindered, secondary face of the macrocycle rather than at the sterically accessible primary face. This is particularly remarkable in light of the relatively small rate constant for $CH_3^{\bullet}$ addition to *rac*-CoL^{2+}, $k = 0.6 \times 10^8$ M^{-1} s^{-1}; this is to be compared to $k = 2.3 \times 10^8$ M^{-1} s^{-1} for $CH_3^{\bullet}$ addition to *meso*-CoL^{2+}.[20,21] We take this to be strong evidence that the dominant form of *rac*-CoL^{2+} is actually five-coordinate prim, *rac*-$CoL(H_2O)^{2+}$ in aqueous solution. Since no ($\leq 10\%$) primary isomer is formed, the rate constant for addition to the primary face of *rac*-CoL^{2+} must be $\leq 0.6 \times 10^7$ M^{-1} s^{-1}. Thus it would appear that water exchange is at least 40 times slower for the primary site of *rac*-$CoL(H_2O)^{2+}$ than for *meso*-$CoL(H_2O)_2^{2+}$ (assuming that the dominant form is six-coordinate, as implicated by structural work on the solid state[22]). This is qualitatively consistent with the trend seen in the crystallographically determined Co(II)-OH_2 distances, 2.25 (5) (primary, *rac*)[9] and 2.482 (5) Å (*meso*).[22]

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Supplementary Material Available: Experimental details of the X-ray diffraction study (Table S1), final thermal parameters for the non-hydrogen atoms (Table S3), calculated and fixed hydrogen atom positions (Table S4), all bond lengths and angles (Table S5), details of hydrogen-bonding interactions (Table S6), and best planes (Table S7) (11 pages); observed and calculated structure factors (Table S2) (12 pages). Ordering information is given on any current masthead page.

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Barrier to Internal Rotation in a Heterometallic Tetrahedrane Cluster. NMR Evidence for Metal Cluster–Aryl Orbital Overlap

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In earlier reports from this laboratory,[2-4] we have demonstrated the utility of ^{13}C NMR spin–lattice relaxation times[5] as a sensitive probe of the electronic and steric factors affecting the internal rotational dynamics of the phenyl groups in benzylidyne- and phosphinidene-capped metal carbonyl clusters.

Several years ago, Schilling and Hoffmann[6] predicted, theoretically, that the barrier to internal rotation of the capping group should be small to nonexistent in trimetallic clusters of the type $[Co_3(CO)_9(\mu_3\text{-}CCR_2)^+]$ (where R = H, alkyl), which contain only terminal carbonyls. We were able to verify this prediction experimentally in a recent NMR relaxation time study[3] of the protonated phenyl carbons in the complex $Co_3(CO)_9(\mu_3\text{-}CPh)$ as a function of temperature in the solvent chloroform. It was observed that "spinning" of the aryl ring about the C–C bond is

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Table I. NMR Relaxation Times and Rotational Diffusion Coefficients in $FeCo_2(CO)_9(\mu_3\text{-}PPh)$ and Related Systems

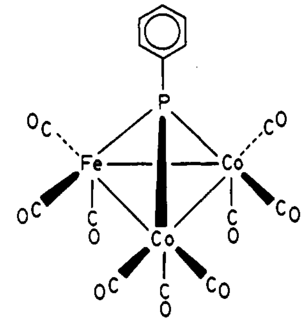
T, K	T_{1O},[a,b] s	T_{1M},[a,b] s	T_{1P},[a,b] s	$D_\perp$,[c] ns^{-1}	$D_S(FeCo_2)$,[c] ns^{-1}	$D_S(Co_3)$,[d] ns^{-1}	$D_S(Bz)$,[e] ns^{-1}
247	1.93 (0.15)	1.76 (0.11)	0.56 (0.06)	2.1	21	4	33
263	2.71 (0.04)	2.39 (0.22)	0.74 (0.01)	2.8	29	5	43
283	3.79 (0.19)	3.64 (0.26)	1.06 (0.09)	4.0	39	8	59
298	4.23 (0.02)	4.30 (0.05)	1.30 (0.13)	4.9	48	10	72
323	5.43 (0.12)	5.70 (0.19)	1.54 (0.04)	5.8	60	14	97

[a] Reported relaxation times are the average of two measurements at each temperature. [b] Quantities in parentheses represent the mean deviations between runs. [c] Diffusion coefficient of $FeCo_2(CO)_9(PPh)$ in chloroform. [d] Diffusion coefficient of $Cp_2Co_3(CO)_4(CPh)$ in chloroform (interpolated by least-squares fit of the data in ref 4 by the Arrhenius equation). [e] Diffusion coefficient of benzene in chloroform.[11]

as rapid as the equivalent rotation of free benzene in the same solvent.

In a still more recent investigation on the temperature dependence of $T_1(^{13}C)$ of the phenyl carbons of $Cp_2Co_3(\mu_2\text{-}CO)(CO)_3(\mu_3\text{-}CPh)$ in chloroform,[4] it was observed that, in marked contrast to the earlier study,[3] the phenyl ring in this complex is completely immobile on a nanosecond time scale.[7] Complementary T_1 measurements on the terminal CO and Cp ligands revealed that the hindrance to internal rotation is not due to phenyl/cyclopentadienyl inter-ring steric repulsions. Rather, it can be attributed to an electronic interaction between the ring's and the bridging carbonyl's π systems first proposed by Stone and co-workers[8] to explain slowed rotation in a similar complex. Its basis is the preferential interaction of the μ_2-CO's π^* orbital with one of the pair of metal 2e orbitals, which in turn removes the degeneracy of the carbynyl's 2p orbitals, leading, ultimately, to an energetically preferred orientation of the phenyl ring parallel to the bridging carbonyl.

Besides the introduction of a μ_2-CO ligand, the substitution of one of the metal centers by a heteroatom will also split the degeneracy of the metals' orbitals and, therefore, may lead, also, to a preferred phenyl group orientation. To determine whether this electronic perturbation is sufficiently strong to affect the ring's rate of internal rotation, we have performed ^{13}C NMR relaxation time experiments on the protonated phenyl carbons of the phosphinidene-capped heterometallic cluster, $FeCo_2(CO)_9(\mu_3\text{-}PPh)$, as a function of temperature in the solvent, $CDCl_3$.



Experimental Section

Phenylphosphine[9] was prepared from dichlorophosphine (Aldrich Chemical), while $FeCo_2(CO)_9(\mu_3\text{-}PPh)$[10] was synthesized according to the procedure of Müller and Vahrenkamp. $CDCl_3$ was distilled from P_2O_5 and stored under argon with Schlenk techniques.[11] The NMR sample was prepared in a 10-mm NMR tube that contained 0.45 g (0.84 mmol) of $FeCo_2(CO)_9(\mu_3\text{-}PPh)$ dissolved in 3.5 mL of $CDCl_3$ (ca. 0.24 M) and was freeze-pump-thaw degassed three times prior to flame sealing.

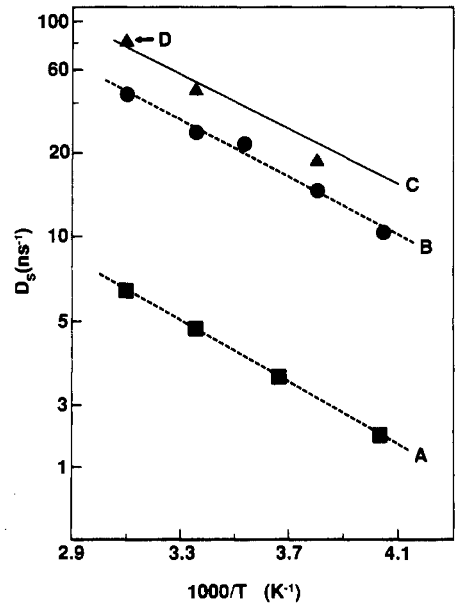


Figure 1. Temperature dependence of the "spinning" diffusion coefficient, D_S: (A) $Cp_2Co_3(\mu_2\text{-}CO)(CO)_3(\mu_3\text{-}CPh)$ (■); (B) $FeCo_2(CO)_9(\mu_3\text{-}PPh)$ (●); (C) benzene (—); (D) $Co_3(CO)_9(\mu_3\text{-}CPh)$ (▲).

^{13}C NMR relaxation time measurements and nuclear Overhauser enhancements were performed at $\nu_0(^{13}C)$ = 75.44 MHz on a Varian VXR-300 NMR spectrometer using the same procedures that were detailed in the earlier investigations.[2-4]

The relaxation times, which are presented in Table I, represent the average of two runs at each temperature. The Overhauser enhancements were found to be complete ($\eta = \eta_{max} = 2.00$), indicating that dipolar interaction with the attached protons is the sole mechanism of ^{13}C relaxation.[12]

Results

As discussed in our earlier investigations, the dipolar relaxation time of the phenyl para carbons in capped clusters can be used to calculate the overall tumbling coefficient, $D_\perp$, of the complex. This value, together with the ratio, T_{1O}/T_{1P} (or T_{1M}/T_{1P}), permits determination of the total "spinning" rate, D_S, of the aryl ring. This latter value is composed of contributions from overall parallel reorientation of the cluster's framework, $D_\parallel$, and internal rotation, R, of the group relative to the skeleton; $D_S = D_\parallel + R$. We note that implicit in the decomposition of the rotational dynamics into parallel and perpendicular diffusion components is the presumption that the molecule's reorientation approximates that of a symmetric top.[5] The structure of the complex and the fact that one observes no systematic deviations between T_{1O} and T_{1M} (Table I) provide evidence that this approximation, required for analysis of the results, is reasonable.[5]

The tumbling and spinning diffusion coefficients of $FeCo_2(CO)_9(\mu_3\text{-}PPh)$ as a function of temperature in chloroform are presented in the fifth ($D_\perp$) and sixth (D_S) columns of Table I. Shown in the latter columns of the table, for comparison (vide infra), are values of D_S for $FeCo_2(CO)_9(PPh)$, $Cp_2Co_3(CO)_4(CPh)$, and benzene.

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(7) It was found in $Cp_2Co_3(\mu_2\text{-}CO)(CO)_3(\mu_3\text{-}CPh)$[4] that the spinning rates, D_S, of the phenyl group and of the Co_3 skeleton are equal to each other, within experimental error. From this, we were able to assign an upper limit to the rate of internal rotation, $R < 1$ ns^{-1}.

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Discussion

It is informative to compare the results of this study with those obtained earlier for $Cp_2Co_3(CO)_4(\mu_3\text{-}CPh)$,[4] in which it was found that an orbital interaction between the ring and bridging carbonyl completely immobilizes the phenyl group on the molecular reorientation (nanosecond) time scale (vide supra). The tumbling rate of the heterometallic cluster is quite close to that of the tricobalt complex; e.g. at 298 K, $D_\perp(FeCo_2) = 4.9\ ns^{-1}$ versus $D_\perp(Co_3) = 4.2\ ns^{-1}$.[4] This result is expected, considering the similar dimensions of the two species. In contrast, as shown in Table I and Figure 1 (lines A and B), the rate of phenyl group spinning in $FeCo_2(CO)_9(\mu_3\text{-}PPh)$ is from 4 to 6 times more rapid than in $Cp_2Co_3(CO)_4(\mu_3\text{-}CPh)$. This shows clearly that there is a substantially lower barrier to internal rotation in the former complex.

To determine whether there is any measurable hindrance to rotation of the phenyl ring, one may compare $D_S(FeCo_2)$ to the rate of the equivalent rotation of free benzene (about its C_2 axis) in chloroform,[13] which we denote as $D_S(Bz)$. As seen in Table I and Figure 1 (lines B and C), the phenyl spinning rate in the complex is somewhat lower, by about 35%, than the rate of rotation of benzene in the same solvent. $D_S(FeCo_2)$ is also below the rotational rate found in an earlier study[3] of the complex, $Co_3(CO)_9(\mu_3\text{-}CPh)$ (points D), where, as noted above, it was found that D_S of the phenyl group is equal to that of benzene, to within experimental error, in agreement with the theoretical calculations of Schilling and Hoffmann.[6]

On the basis of the above comparisons, it appears that the replacement of $Co(CO)_3$ and a μ_3-CPh fragment with $Fe(CO)_3$ and a μ_3-PPh fragment, respectively, does induce an electronic perturbation in the metal's orbitals that leads to a small, but finite barrier to internal rotation of the capping phenyl group. However, it is clear, too, that this barrier is much smaller than that found in earlier investigations of carbonyl bridged clusters.[4,8] In addition, we must add the caveat that it is possible, but not likely, that the relatively small hindrance to ring rotation might be attributable, instead, to another effect such as preferential solvation of the phenyl group in $FeCo_2(CO)_9(\mu_3\text{-}PPh)$, although this was not seen in the previous investigation of $Co_3(CO)_9(\mu_3\text{-}CPh)$.

Further investigations of carbonyl-bridged and heterometallic species will be necessary to fully assess the factors influencing the magnitude of electronic barriers in metal carbonyl clusters.

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Aerobic Photooxidation of Substituted Benzenes Catalyzed by the Tungsten Isopolyanion $[W_{10}O_{32}]^{4-}$

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Inorganic, soluble iso- and heteropolyanion oxides[1] are promising candidates for the functionalization of organic compounds. Very recent work has shown that the decatungstate anion, $[W_{10}O_{32}]^{4-}$ (W10), in particular may behave as an efficient, stable, selective photooxidation catalyst.[2-7]

Under anaerobic conditions W10 selectively promotes the dimerization of several olefins[2] and the dehydrogenation of alkanes to alkenes,[3] reoxidation of the reduced catalyst occurring at the expense of hydrogen ions. Although the yields are not particularly high, one distinct advantage of W10 is its high quantum yield efficiency, with measured values which may approach unity, when mineral acids are added to the reaction mixture.[3]

Preliminary reports[5-7] suggest that, under aerobic conditions, W10 promotes the oxidation of saturated hydrocarbons, notably branched ones containing tertiary carbon atoms. By use of a classical autoxidation mechanism, alkyl hydroperoxides or oxygenated products deriving from their further reactivity are obtained in moderate yields. No information is available concerning the related hexatungstate anion $[W_6O_{19}]^{2-}$ (W6).

Following our previous interest in this field,[8,9] we now report new results concerning the ability of W10 to catalyze the aerobic photooxidation of various alkylbenzenes. Experimental data showing W6 or its V(V)-substituted derivative to be totally inactive toward such oxidations are also presented.

Experimental Section

Materials. $[Bu_4N]_4W_{10}O_{32}$ and $[Bu_4N]_3VW_5O_{19}$ were prepared and purified according to published methods.[10,11] The synthesis of $[Bu_4N]_2W_6O_{19}$, reported in the literature,[12] was modified by using the much easier procedure given below. Commercially available alkylbenzenes (Fluka, purity ≥99%) were used as received. Acetonitrile was freshly distilled from CaH_2 under a stream of prepurified nitrogen.

Measurements. Elemental analyses were performed by H. Malissa Analitische Laboratorium, Elbach, FRG. IR and electronic spectra were recorded, respectively, on Perkin-Elmer 983G and Perkin-Elmer 330 spectrophotometers. Qualitative and quantitative product analysis was accomplished by GC, eventually coinjecting authentic samples, using a Perkin-Elmer 8500 gas cromatograph equipped with a packed column (length 2 m, filling 5% Carbowax on Chromosorb W80/100) and with an HP 3390A integrator.

Synthesis of $[Bu_4N]_2W_6O_{19}$. $Na_2WO_4{\cdot}2H_2O$ (6.0 g, 18.0 mmol) was dissolved in boiling CH_3CN (150 mL). Acidification was performed by addition of a boiling solution of HCl 12 N (2.5 mL) in water (200 mL). After a few minutes of stirring, Bu_4NCl (1.78 g, 6.0 mmol) dissolved in water (20 mL) was added dropwise to the pale yellow solution. After cooling, the white, crystalline precpitate was filtered out, washed with ethanol and ether, and crystallized from a small amount of CH_3CN (5 mL). Yield: 2.29 g (41%). Anal. Calcd for $C_{32}H_{72}N_2W_6O_{19}$: C, 20.31; H, 3.84; N, 1.48; W, 58.30. Found: C, 20.26; H, 3.85; N, 1.45; W, 58.05. UV-vis (CH_3CN): λ_{max} 280 nm (ϵ 1.18×10^4 $dm^3/(mol{\cdot}cm)$).

Photochemical Oxidations. Aerobic reactions were performed in a homemade immersion reactor by dissolving the substrate (12.5 mmol) and the required amount of catalyst in 100 mL of CH_3CN. A 125-W high-pressure mercury lamp, in conjunction with a cold-water Pyrex cutoff filter ($\lambda \geq 320$ nm), was used as a source of irradiation. The reaction solutions were kept under a constant, slight overpressure of pure dry oxygen or air and thoroughly stirred and thermostated at 25 °C (if not otherwise stated). Sampling and analyses were performed at 1- and 2-h intervals.

Results and Discussion

This note describes the aerobic, catalytic photooxidation of various alkylbenzenes in the presence of $[W_{10}O_{32}]^{4-}$ and related tungsten isopolyanions. The basic reaction investigated is

$$\mathrm{PhR} + O_2 \xrightarrow[h\nu,\ CH_3CN,\ 25\ ^\circ C]{\text{POA catalyst}} \text{carbonyl derivative} + \text{carboxylic acid} + \text{minor products}$$

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