planes make a dihedral angle of 11.0°, and these interactions appear weaker than those observed in the [Cu(L-glu)(*o*-phen)H_2O]·3H_2O complex,[2] where the dihedral angle between aromatic ring planes is 1.4°.

The complex is stable in air and presents a thermogravimetric behavior corresponding to the loss of uncoordinated and coordinated water molecules in the 35–120 °C temperature range. In the square-pyramidal [Cu(L-glu)(*o*-phen)H_2O]·3H_2O complex[2] the coordinated water molecule is lost in the 110–150 °C temperature range, indicating a greater bond strength of the coordinated water molecule in a square-pyramidal than in a tetragonally distorted octahedral environment.

The room-temperature magnetic moment of the complex (μ_{eff}(293 K = 1.84 μ_B) is "normal" and typical of "magnetically dilute" complexes;[21] its polycrystalline EPR spectrum ($g_\parallel$ = 2.33; $g_\perp$ = 2.08) closely resembles those of copper(II) complexes having similar environments and chromophores, reported in the literature,[21,22] for which an essentially $d_{x^2-y^2}$ ground state has been suggested.

The room-temperature electronic spectrum of the complex presents a broad d–d band with an unsymmetrical maximum centered at 16 400 cm^{-1}, typical of CuN_3O_3 chromophores.[23,24]

Acknowledgment. We are grateful to the Centro di Calcolo Elettronico dell'Università di Modena for computing support and to the Centro Strumenti dell'Università di Modena for recording EPR spectra.

Registry No. [Cu(L-asp)(*o*-phen)H_2O]·4H_2O, 102649-32-1.

Supplementary Material Available: Listings of atomic temperature factors, hydrogen atom parameters, complete bond distances and angles, hydrogen-bonding distances and angles, ring-stacking interactions, and selected least-squares planes (7 pages). Ordering information is given on any current masthead page.

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Contribution from the Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464, Japan

Kinetic Study of Acetic Acid Exchange on Manganese(II), Cobalt(II), and Copper(II) Acetates in Acetic Acid by Oxygen-17 Nuclear Magnetic Resonance[1]

Akiharu Hioki,† Shigenobu Funahashi,* and Motoharu Tanaka

Received October 2, 1985

We have previously studied acetic acid exchange on perchlorates of manganese(II), iron(II), cobalt(II), nickel(II), and copper(II) ions in acetic acid (HOAc).[2] These metal(II) perchlorates in acetic acid exist as hexasolventometal ions that form ion pairs with perchlorate anion. On the other hand, acetate ion (OAc^-) in transition-metal(II) acetates is bound to the central metal ions in acetic acid.[3,4] Thus, we expect that coordinated acetate ion exerts some effect on the solvent-exchange rate, i.e., bound-ligand effect. In this work rates of acetic acid exchange on $Mn(OAc)_2$, $Co(OAc)_2$, and $Cu_2(OAc)_4$ (tetrakis(μ-acetato)dicopper(II)) in acetic acid and mixtures with dichloromethane-d_2 as an inert cosolvent were measured by means of the oxygen-17 NMR line-broadening method. The activation parameters obtained are compared with those for the corresponding perchlorates.[2]

Experimental Section

The purification of acetic acid and dichloromethane-d_2 (CD_2Cl_2) and the preparation of oxygen-17-enriched acetic acid were described previously.[2,5-8] The percentage of oxygen-17 in the oxygen-17-enriched acetic acid is 5.13 atom % of all oxygen atoms. The mean molecular weight of this oxygen-17-enriched acetic acid is 60.53. Tetrasolventomanganese(II) acetate was prepared by adding the stoichiometric amount of acetic anhydride to the tetrahydrate dissolved in acetic acid and allowing the reaction to occur at room temperature for 2 weeks.[4] The obtained crystal was washed with acetic anhydride and acetic acid. The resultant pale pink compound may be formulated as $Mn(OAc)_2(HOAc)_4$. The compound, dried in a desiccator over sodium hydroxide for 1 week under reduced pressure, should be $Mn(OAc)_2(HOAc)$, which was confirmed by the analysis for manganese (calcd, 23.57%; found, 23.55%). Hydrated cobalt(II) acetate (reagent grade) was recrystallized from distilled water. The hydrate was dissolved in acetic acid. In order to eliminate the water, excess acetic anhydride was added to the cobalt(II) acetate solution. After this solution was allowed to stand at 80 °C for 3 days, anhydrous cobalt(II) acetate precipitated. This red crystal was recrystallized from acetic acid and may be formulated as $Co(OAc)_2(HOAc)_4$. The crystals were dried at 120 °C for 3 h to obtain $Co(OAc)_2$. The quantitative change of $Co(OAc)_2(HOAc)_4$ to $Co(OAc)_2$ was confirmed thermogravimetrically (Shimadzu thermal analyzer DT-30). Tetrakis(μ-acetato)dicopper(II) disolvate ($Cu_2(OAc)_4(HOAc)_2$, dimeric copper(II) acetate) was prepared as described previously.[5] It was dried in a desiccator over sodium hydroxide for a few days under a reduced pressure. The determination of copper in the dried copper(II) acetate crystals by both electrolysis and EDTA titration confirmed the composition of $Cu_2(OAc)_4$.

^{17}O NMR spectra were obtained with use of JNM-FX60, JNM-FX90QE, and JNM-GX400 (JEOL Ltd.) instruments operating at 8.16, 12.15, and 54.21 MHz, respectively. ^1H NMR spectra were observed at 60 MHz on a JNM-C-60H NMR spectrometer (JEOL Ltd.). The preparation of NMR samples and the NMR measurement have been described in our previous paper.[8] The compositions of samples for the NMR measurement are tabulated in Table I.

The temperature dependence of the observed transverse relaxation rate, $1/T_{2P}$, corrected for the ligand relaxation rate in the absence of the metal complex, can be analyzed by the modified Swift and Connick equation (eq 1),[9-11] where symbols have the usual meaning.[8] The analysis of data was carried out by the least-squares program SALS.[12]

$$(T_{2P}P_M)^{-1} = \frac{1}{\tau_M}\frac{T_{2M}^{-2} + (\tau_M T_{2M})^{-1} + (\Delta\omega_M)^2}{(\tau_M^{-1} + T_{2M}^{-1})^2 + (\Delta\omega_M)^2} + \frac{1}{T_{2O}} \quad (1)$$

Results

All NMR data for line broadening are tabulated in Tables s-I and s-II (supplementary material).

Manganese(II) Acetate. The temperature dependence of line widths log $(T_{2P}P_M)^{-1}$ for manganese(II) acetate is represented in Figure 1. It is reasonable that the chemical-exchange region, where τ_M^{-1} contributes to the line width to a large extent, is identical at 8.16, 12.15, and 54.21 MHz for the sample of 20.4 wt % HOAc. NMR and kinetic parameters for a nonlinear least-squares fitting are given in Table s-III (supplementary

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Table I. Compositions of Sample Solutions

soln	species	$[M]/m^a$	$[HOAc]/m$	$[CD_2Cl_2]/m$	P_M	wt % of HOAc
A0	ref soln	0	16.52	0	0	100.0
A1m	$Mn(OAc)_2$	4.84×10^{-3}	16.52	0	8.78×10^{-4}	100.0
A2o	$Co(OAc)_2$	1.44×10^{-2}	16.52	0	2.62×10^{-3}	100.0
A3u	$Cu_2(OAc)_4$	1.11×10^{-2} [b]	16.52	0	6.75×10^{-4}	100.0
A4u	$Cu_2(OAc)_4$	2.30×10^{-2} [b]	16.52	0	1.40×10^{-3}	100.0
B0	ref soln	0	3.37	9.16	0	20.4
B1m	$Mn(OAc)_2$	2.30×10^{-4}	3.37	9.16	2.06×10^{-4}	20.4
B2o	$Co(OAc)_2$	3.32×10^{-3}	3.37	9.16	2.97×10^{-3}	20.4
B3o	$Co(OAc)_2$	6.63×10^{-3}	3.37	9.16	5.96×10^{-3}	20.4
B4u	$Cu_2(OAc)_4$	2.74×10^{-2} [b]	3.37	9.16	8.25×10^{-3}	20.4
B5u	$Cu_2(OAc)_4$	2.95×10^{-2} [b]	3.37	9.16	8.90×10^{-3}	20.4
B6u	$Cu_2(OAc)_4$	4.72×10^{-2} [b]	3.37	9.16	1.44×10^{-2}	20.4
C0[c]	ref soln	0	0.79	11.0	0	4.8
C1m[c]	$Mn(OAc)_2$	1.96×10^{-4}	0.79	11.0	9.87×10^{-4}	4.8

[a] m is in the unit of mol kg^{-1}. [b] Concentration as dimer for $Cu_2(OAc)_4$. [c] Solution C was used for measuring the hydroxyl proton NMR.

Table II. Rate Constants and Activation Parameters for Acetic Acid Exchange

metal species	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J mol^{-1} K^{-1}	$k(25\ °C)/s^{-1}$	concn of HOAc/ wt %	remarks
$Mn(OAc)_2$	32 ± 3	9 ± 11	$(4.8 \pm 0.9) \times 10^7$	20.4	this work
$Mn(ClO_4)_2$	29 ± 2	−10 ± 7	$(1.6 \pm 0.1) \times 10^7$	4.94, 20.0, 100	ref 2 (^{17}O)
$Co(OAc)_2$	37 ± 3	14 ± 12	$(9.9 \pm 3.3) \times 10^6$	20.4	this work
$Co(ClO_4)_2$	37 ± 3	−6 ± 12	$(1.3 \pm 0.2) \times 10^6$	20.0	ref 2 (^{17}O)
$Cu_2(OAc)_4$	51 ± 5	18 ± 15	$(6.3 \pm 1.0) \times 10^4$	100	this work
$Cu_2(OAc)_4$	51 ± 2	12 ± 6	$(2.8 \pm 0.1) \times 10^4$	20.4	this work
$Cu_2(OAc)_4$	53 ± 4	13 ± 8	$(1.7 \pm 0.2) \times 10^4$	24.1	ref 5 (^1H (CH_3))
$Cu_2(OAc)_4$	51 ± 4	3 ± 8	$(1.2 \pm 0.2) \times 10^4$	9.8	ref 5 (^1H (CH_3))
$Cu_2(OAc)_4$	53 ± 4	10 ± 8	$(9.4 \pm 1.1) \times 10^3$	4.3	ref 5 (^1H (CH_3))
$Cu(ClO_4)_2$			$\simeq 1 \times 10^7$ [a]	4.94, 20.0	ref 2 (^{17}O)

[a] At −25 °C.

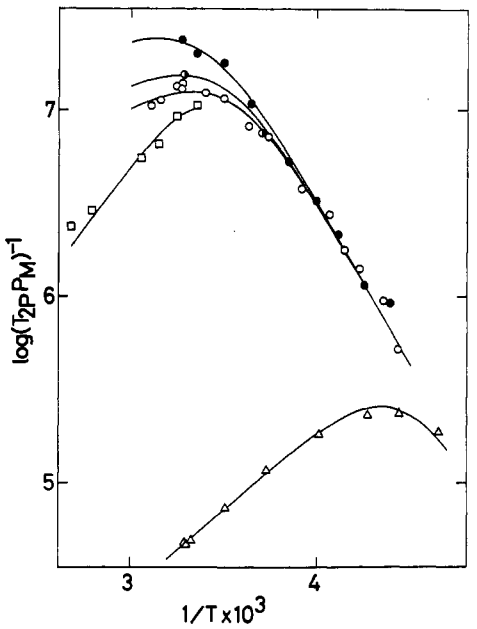

Figure 1. Temperature dependence of log $(T_{2P}P_M)^{-1}$ for the hydroxyl proton and the oxygen-17 of bulk acetic acid in the presence of $Mn(OAc)_2$: □, oxygen-17 of solution A1m at 8.16 MHz; ○, oxygen-17 of solution B1m at 8.16 MHz; ◑, solution B1m at 12.15 MHz; ●, solution B1m at 54.21 MHz; △, hydroxyl proton of solution C1m at 60.0 MHz. The curves in Figures 1–3 were calculated with the NMR and kinetic parameters obtained.

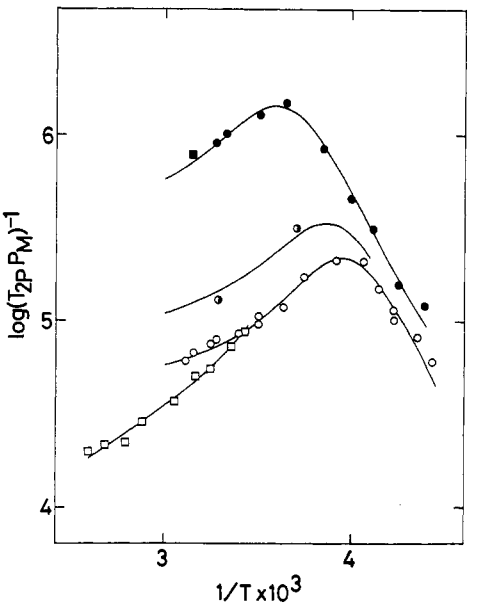

Figure 2. Temperature dependence of log $(T_{2P}P_M)^{-1}$ for the oxygen-17 of bulk acetic acid in the presence of $Co(OAc)_2$: □, solution A2o at 8.16 MHz; ■, solution A2o at 54.21 MHz; ○, solutions B2o and B3o at 8.16 MHz; ◑, solution B3o at 12.15 MHz; ●, solution B3o at 54.21 MHz.

material). The rate constants and activation parameters obtained are summarized in Table II. For the sample of 100 wt % HOAc the contribution of chemical exchange to log $(T_{2P}P_M)^{-1}$ is relatively small due to the relatively high freezing point (16.6 °C) of acetic acid. However, these data are consistent with the activation parameters obtained for the sample of 20.4 wt % HOAc. Data of the hydroxyl proton for the sample of 4.8 wt % HOAc seem also to agree satisfactorily with the activation parameters obtained by ^{17}O NMR.

For oxygen-17 NMR at the higher temperature range $1/T < 3.5 \times 10^{-3}$ K^{-1}, the value of log $(T_{2P}P_M)^{-1}$ at 54.21 MHz is larger than that at 8.16 MHz. Since the T_{2M}^{-1} term for oxygen-17 is attributable to the hyperfine interaction, the longitudinal relaxation time of the electron depends on the observed frequency as in the case of $Mn(ClO_4)_2$.[2,10,13]

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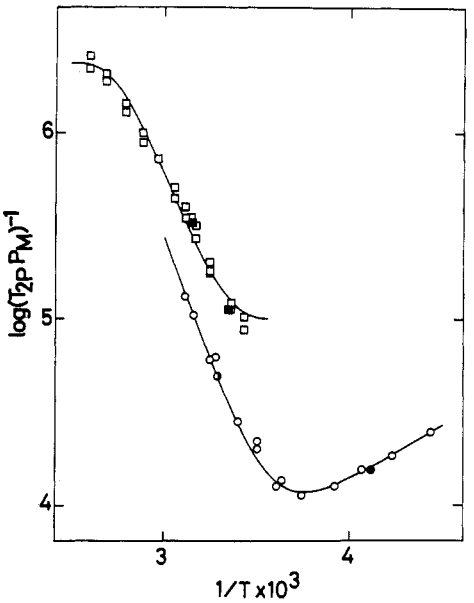


Figure 3. Temperature dependence of log $(T_{2P}P_M)^{-1}$ for the oxygen-17 of bulk acetic acid in the presence of $Cu_2(OAc)_4$: □, solutions A3u and A4u at 8.16 MHz; ■, solution A3u at 54.21 MHz; ○, solutions B4u, B5u, and B6u at 8.16 MHz; ◐, solution B4u at 12.15 MHz; ●, solution B6u at 54.21 MHz.

Cobalt(II) Acetate. The temperature dependence of line widths log $(T_{2P}P_M)^{-1}$ of ^{17}O NMR for cobalt(II) acetate is presented in Figure 2. Data at 12.15 MHz are not inconsistent with the activation parameters (given in Table II) obtained for the other two observed frequencies (8.16 and 54.21 MHz). For the sample solution of 100 wt % HOAc the chemical-exchange region was not observed above the freezing point of the solution (16.6 °C). No ^1H NMR line broadening was observed within the limited solubility of $Co(OAc)_2$.

At the higher temperature range $1/T < 4 \times 10^{-3}$ K^{-1} the line widths depend greatly on the frequencies. This results from the contribution of $\Delta\omega_M$. The scalar coupling constant $(A/\hbar)$ is calculated to be 4.6×10^7 rad s^{-1}.

Copper(II) Acetate Dimer. In Figure 3 is given the temperature dependence of line widths of ^{17}O NMR for the copper(II) acetate dimer. τ_M^{-1} and T_{2O}^{-1} do not depend on observed frequencies at all. The activation parameters for the acetic acid exchange on the copper(II) acetate dimer are listed in Table II together with those obtained by ^1H NMR.[5]

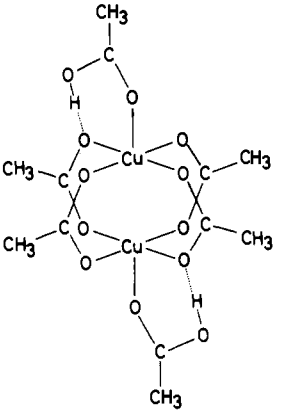
Discussion

In acetic acid with low dielectric constant, we should consider separately the ionization and dissociation steps. Dissociation of the 1:1 electrolyte AB is expressed as

$$AB \overset{K_i}{\rightleftharpoons} A^+B^- \overset{K_d}{\rightleftharpoons} A^+ + B^-$$

Overall dissociation constants K_D $(=[A^+][B^-]/([AB] + [A^+B^-]) = K_iK_d/(1 + K_i))$ for metal(II) acetates $(M(OAc)_2 \rightleftharpoons M(OAc)^+ + OAc^-)$ are available.[4] K_D values are $10^{-7.53}$ mol dm^{-3} for $Mn(OAc)_2$ and $10^{-7.56}$ mol dm^{-3} for $Co(OAc)_2$. K_d is calculated to be about 10^{-6} mol dm^{-3} for these 1:1 electrolytes by an equation of the type derived by Fuoss and Kraus.[14] Judging from the K_i values, which are estimated to be $10^{-1.53}$ for $Mn(OAc)_2$ and $10^{-1.56}$ for $Co(OAc)_2$, it may be concluded that two OAc^- ions in each acetate salt exist in the inner sphere of the metal(II) ion. This is also supported by our studies on the equilibria and kinetics of some metal(II) acetates in acetic acid.[6,15-17] From vapor pressure measurements, the van't Hoff coefficients of the manganese(II) and cobalt(II) acetates were determined to be unity and that of copper(II) acetate was one-half.[15] Therefore, copper(II) acetate exists as a dimer, while the other acetates are monomeric in acetic acid. Solubilities of manganese(II) and cobalt(II) acetates were measured to investigate the aquation of these metal acetates, and the equilibrium of copper(II) acetate with water was studied by cryoscopy.[15] Judging from these findings, there is no effect of H_2O under the present experimental conditions, because the amount of water in the present systems is at most less than 10^{-3} mol kg^{-1}. The equilibrium constants for reaction of copper(II) acetate with hydrochloric acid, perchloric acid, lithium chloride, and lithium acetate were determined by means of spectrophotometry.[6,16] Kinetic studies on reactions of the copper(II) acetate dimer with lithium chloride and hydrogen chloride have elucidated their reaction mechanisms.[17] The strongest acid is perchloric acid although it forms an ion pair in acetic acid. The addition of the stoichiometric amount of $HClO_4$ to the $M(OAc)_2$ solution gives the corresponding $M(ClO_4)_2$ solution.

There have been some studies on the monomer–dimer equilibrium of copper acetate as a function of the water concentration in acetic acid.[17-19] Under our experimental conditions copper(II) acetate should exist solely as a dimer. According to Grasdalen,[20] in ethanol solution the ethanol molecules coordinated to the dimeric copper acetate at its axial position are readily replaced by addition of acetic acid. This is contrary to the prediction based on the difference in the basicity between acetic acid and ethanol: the latter is much more basic than the former. Moreover, in the ^1H NMR spectra of mixed solvents involving both ethanol and acetic acid in the presence of the dimeric copper acetate, the ethanol signals are the same as those of pure ethanol while the HOAc signals are very broad and shifted. These facts point to a strong interaction of acetic acid with the copper species. The geometry should thus favor the coordination of acetic acid by an extra hydrogen bonding with the bridging acetate as I.



I

As apparent from Table II, the exchange rates for $Mn(OAc)_2$ and $Co(OAc)_2$ are obviously higher than those for $Mn(ClO_4)_2$ and $Co(ClO_4)_2$, respectively. This enhancement of exchange rate seems to result from an electron donation from coordinated acetate ions to the central metal(II) ion.[21]

As can be seen from Table II, the activation parameters for acetic acid exchange on the copper(II) acetate dimer obtained from ^{17}O NMR are in good agreement with those from ^1H NMR reported previously,[5] although the acetic acid concentration ranges from 4.3 wt % (0.72 mol kg^{-1}) to 100 wt % (17 mol kg^{-1}). As proposed previously,[5] this solvent exchange corresponds to acetic acid exchange with a dissociative activation mode at the axial sites of tetrakis(μ-acetato)dicopper(II). The solvent exchange on

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hexasolventocopper(II) ion in acetic acid is very fast, as expected from the Jahn–Teller effect of the copper(II) ion,[2] while the solvent-exchange rate on the copper acetate is much slower, since the latter forms the dimeric structure and the solvated acetic acid molecules at its axial sites are stabilized by hydrogen bonding as depicted in I.

Acknowledgment. The present work was supported through a Grant-in-Aid for Scientific Research (No. 59430010) and a Grant-in-Aid for Special Project Research (No. 60129031) from the Japanese Ministry of Education, Science, and Culture.

Registry No. HOAc, 64-19-7; $Mn(OAc)_2$, 638-38-0; $Co(OAc)_2$, 71-48-7; $Cu_2(OAc)_4$, 23686-23-9.

Supplementary Material Available: Oxygen-17 line-broadening data for $Mn(OAc)_2$, $Co(OAc)_2$, and $Cu_2(OAc)_4$ in acetic acid and in mixtures with CD_2Cl_2 (Table s-I), proton line-broadening data for $Mn(OAc)_2$ in an acetic acid–CD_2Cl_2 mixture (Table s-II), and values of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, C_M, E_M, C_O, E_O, and C_ω (Table s-III) (5 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, University of Hamburg, D-2 Hamburg 13, FRG

Ring-Substituted Derivatives of η^5-$C_5H_5V(CO)_4$: Synthesis and ^{51}V NMR Spectroscopic Characteristics

Martin Hoch, Andreas Duch, and Dieter Rehder*

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In a recent paper,[1] Basolo and co-workers described the synthesis and molecular structure of η^5-$C_9H_7V(CO)_4$ (**1**) (C_9H_7 = indenyl), obtained in 40% yield from the reaction of $[V(CO)_6]^-$ and C_9H_7HgCl. We have found that the direct action of the neutral 17-electron complex $V(CO)_6$ on indene produces **1** in about 70% yield. This reaction, which possibly runs via an intermediate "$HV(CO)_6$",[2] can more generally be applied to the synthesis of other ring-substituted cyclopentadienyl complexes in yields of 55–85% and thus opens a route to this little known class of compounds alternative to the hydride transfer from phosphine-stabilized hydridocarbonylvanadium complexes to the exocyclic carbon of pentafulvenes.[3] Ring-substituted derivatives of $C_5H_5V(CO)_4$ are of considerable interest in the context of the stabilization of the labile $C_5H_5V(CO)_3THF$, an excellent precursor for the synthesis of a large variety of substitution products $C_5H_5V(CO)_3L$.[4]

Experimental Section

All operations were carried out under nitrogen and in oxygen-free, absolute solvents. Bis(cyclopentadienes), as far as available commercially ($(C_5H_6)_2$, $(C_5Me_5)_2$, $(C_5(Et)Me_4H)_2$, $(C_5Me_5H)_2$) and indene were purified by distillation. Silica gel (Kieselgel 60, Merck, 70–230 mesh ASTM) was pretreated in vacuo (8 h, 1–2 Torr) and loaded with N_2.

Preparation of Alkylcyclopentadienes. The equivalent of 2.4 g of sodium hydride (77 mmol) of a paraffin oil suspension of NaH was washed twice with 20-mL portions of light petroleum ether, dried in vacuo, treated with 100 mL of THF, and cooled in an ice bath. A 77-mmol sample (ca. 5 g or 6.4 mL) of freshly distilled $C_5(R)H_5$ (R = H, Me) was added so as to keep the evolution of H_2 at a moderate rate. In case the solution was still turbid, further cyclopentadiene was added in small portions until clearing. To this colorless to pink solution was added 65 mmol of alkyl halide (CyBr or CyCl, (cetyl)Br, (trityl)Cl). After ca. 2 h of refluxing, the yellow to light red solution was evaporated, the remaining oil or paste redissolved in 100 mL of diethyl ether, and the resultant solution washed four times with 10-mL portions of water. The organic phase was then dried over $MgSO_4$ and the ether removed by distillation. Workup of the residual products was carried out by fractional distillation ($C_5Me(Cy)H_4$, 80–85 °C at 15–18 Torr; yield 60%), by filtration of the ether solution through a 6-cm layer of silica gel ($C_5Me(cetyl)H_4$;[5] yield 85%), or by recrystallization from petroleum ether[6] ($C_5(trityl)H_5$; yield 85%). Only the cyclohexyl derivative tends to dimerize.

$V(CO)_6$ was obtained in 91% yields by reacting 9-g portions of Na(diglyme)$_2$V(CO)$_6$ (Ventron) with 18 g of orthophosphoric acid, intimately mixed in a sublimation apparatus. $V(CO)_6$ sublimes from this mixture at 50 °C and 0.01 Torr.

η^5-Cp′V(CO)$_4$. In a typical experiment, 310 mg (1.4 mmol) of $V(CO)_6$, dissolved in 25 mL of *n*-hexane, was treated with 1.7 mmol of the freshly distilled cyclopentadiene and the mixture refluxed for 2 h. Direct sunlight was avoided. In *n*-pentane, reaction times are about 3 times as long. Small amounts of vanadium metal and $[Cp'_2V(CO)_2][V(CO)_6]$ were filtered off. The filtrate, appearing orange or green (the latter due to suspended vanadium particles) and containing $Cp'V(CO)_4$ and $(HCp')_n$ (^1H NMR evidence), was evaporated to yield an oil. This was dissolved in 1 mL of THF and chromatographed on silica gel with pentane as elutant (column dimensions 10 × 25 cm; ca. 60 mL of pentane; elution time ca. 1 h). After removal of the pentane by vacuum evaporation at room temperature, the complexes were obtained in a pure form and with satisfactory elemental analyses. Yields and some of the properties of the new compounds are given in Table I.

Table I. Yields and Selected Properties of η^5-Cp′V(CO)$_4$ Complexes

complex	Cp′[a]	yield, %	properties
1	indenyl	69	orange crystals
2	C_5(trityl)H_4	85	yellow crystals
3	C_5Me_5	73	orange powder
4	$C_5(Et)Me_4$	72	orange powder
5	C_5Me(cetyl)H_3	58	light yellow wax
6	$C_5Me(Cy)H_3$	54	orange crystals
7	C_5MeH_4	76	orange oil

[a] Abbreviations: indenyl = C_9H_7, trityl = $C(C_6H_5)_3$, cetyl = n-$C_{16}H_{33}$, Cy = c-C_6H_{11}.

Results and Discussion

The compounds described in this work and obtained according to eq 1 are given in Table II together with their characteristic vanadium-51 NMR shifts and CO stretching frequencies. In

$$V(CO)_6 + HCp' \rightarrow Cp'V(CO)_4 + 2CO\ (+{}^1/_2H_2) \quad (1)$$

contrast to findings on (acetyl–C_5H_4)V(CO)$_4$[7] and various (alkenyl–C_5H_4)V(CO)$_4$ complexes,[2] **3**, **4**, **6**, and **7** show two IR-active bands only. The B_1 mode, which should gain intensity as the overall C_{4v} symmetry of the parent cyclopentadienyl complex decreases, arises as a weak shoulder in the case of **1**, **2**, and **5**. No splitting of the E mode[7] was observed. The absence of the B_1 band in most of the complexes $Cp'V(CO)_4$ shows that the effective local symmetry is still C_{4v}; i.e. there are no rotational barriers for Cp′ at room temperature. Compelxes **1**, **4**, and **5** have also been characterized by their mass spectra,[8] showing a frag-

(1) Kowalewski, R. M.; Kipp, D. O.; Stauffer, K. J.; Swepston, P. N.; Basolo, F. *Inorg. Chem.* **1985**, *24*, 3750.
(2) Hoffmann, K.; Weiss, E. *J. Organomet. Chem.* **1977**, *131*, 273.
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(5) $n^{18.5}D$ 1.4702; melting range 10–14 °C.
(6) Hartmann, H.; Flenner, K.-H. *Z. Phys. Chem.* (*Liepzig*) **1950**, *194*, 278.
(7) Palyi, G.; King, R. B. *Inorg. Chim. Acta* **1975**, *15*, L23.
(8) Selected peaks, *m/e* (relative intensities in parentheses), are as follows: (indenyl)V(CO)$_4$: 278 (7), $C_9H_7V(CO)_4$; 250 (10), $C_9H_7V(CO)_3$; 222 (12), $C_9H_7V(CO)_2$; 194 (10), $C_9H_7V(CO)$; 166 (100), C_9H_7V; 140 (11), C_7H_5V; 115 (24), C_9H_7; 89 (7), C_7H_5; 76 (7), C_6H_4; 65 (15), C_5H_5. {(Et)Me$_4$C$_5$}V(CO)$_4$: 312 (52), (Et)Me$_4$CpV(CO)$_4$; 284 (46), (Et)Me$_4$(CpV(CO)$_3$; 256 (31), (Et)Me$_4$CpV(CO)$_2$; 228 (68), (Et)Me$_4$CpV(CO); 200 (100), (Et)Me$_4$CpV; 185 (45), possibly η-$C_6Me_5H_2V$; 184 (90), likely corresponding to {η^6-C_6Me_5H}V, a plausible fragment of [(η^6-arene)V(CO)$_4$]$^+$ (Calderazzo, F.; Pampaloni, G.; Vitale, D.; Zanazzi, P. F. *J. Chem. Soc., Dalton Trans.* **1982**, 1993)); 51 (65), V; metastable peaks 175.4 ($EtMe_4CpV(CO)^{\cdot+} \rightarrow EtMe_4CpV^{\cdot+}$ + CO), 169.3 ($EtMe_4CpV^{\cdot+} \rightarrow C_6Me_5HV^{\cdot+} + CH_4$). {Me(cetyl)H$_3C_5$}V(CO)$_4$: 466 (2), Me(cetyl)CpV(CO)$_4$; 438 (1), Me(cetyl)CpV(CO)$_3$; 410 (1), Me(cetyl)V(CO)$_2$; 382 (2), Me(cetyl)V(CO); 354 (43), Me(cetyl)V; 303 (100), Me(cetyl)Cp; 70 (7), C_5H_{10}; 56 (41), C_4H_8; 42 (79), C_3H_4. The following peaks correspond to the fragmentation pattern of the cetyl fragment c-{C_3(Me)H}(CH$_2$)$_n$CH$_3$ (*n* and the relative intensities are given in parentheses): 178 (*n* = 9; 2), 164 (*n* = 8; 6), 150 (*n* = 7; 7), 136 (*n* = 6; 16), 122 (*n* = 5; 23), 108 (*n* = 4; 77), 94 (*n* = 3; 80).

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