Communications

Formation and Structure of Tetracarbonylvanadium Half-Sandwich Complexes: Tetracarbonyl(η^5-*sec*-butylmethylcyclopentadienyl)vanadium(I) and *meso*-[(1,1′,2,2′,2a,2a′,8b,8b′,8a,8a′-η^5,η^5)-3,3′-Biacenaphthylenyl]octacarbonyldivanadium(I)

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Summary: V(CO)$_6$ reacts with acenaphthylene to form a double half-sandwich complex with, according to the single-crystal X-ray structure analysis, a bis(η^5) coordination and an exo–exo connection of the two halfs of the molecule. In solution, exo–exo and endo–endo forms are present (^{51}V NMR evidence). The ^{51}V NMR spectrum of [η^5-C_5H_3(Me)*s*-Bu]V(CO)$_4$ reveals the presence of two diasteromeric pairs of enantiomers for each of the two positional (1,2 and 1,3) isomers.

^{51}V NMR spectroscopy is a powerful tool for the detection of closely related species distinct with respect to electronic and/or steric factors.[1] We wish to report on the application of this method to chiral compounds belonging to the only sparingly investigated family of half-sandwich complexes containing the carbonylvanadium moiety. We present a general synthetic scheme, exemplified for the preparation of a mono- and a dinuclear half-sandwich with two and four elements of chirality, respectively. We support our results by an X-ray analysis of one of the meso forms of the latter.

The reaction between hexacarbonylvanadium (1) and substituted cyclopentadienes, $\overline{\mathrm{Cp}}$H, such as *sec*-butylmethylcyclopentadiene,[2] yields a mixture of oxidation product 2 and disproportionation product 3 (Scheme I). This reaction type, which is applicable quite generally to various $\overline{\mathrm{Cp}}$H,[3] can be optimized to yields up to 80% of the half-sandwich complex $\overline{\mathrm{Cp}}$V(CO)$_4$. Compound 2 has a center and a plane of chirality. Hence, for each of the two positional isomers (1,2, **2a**; 1,3, **2b**), we expect two diastereomeric pairs of enantiomers, and these can, in fact, be observed in the ^{51}V NMR solution spectrum (Figure 1).

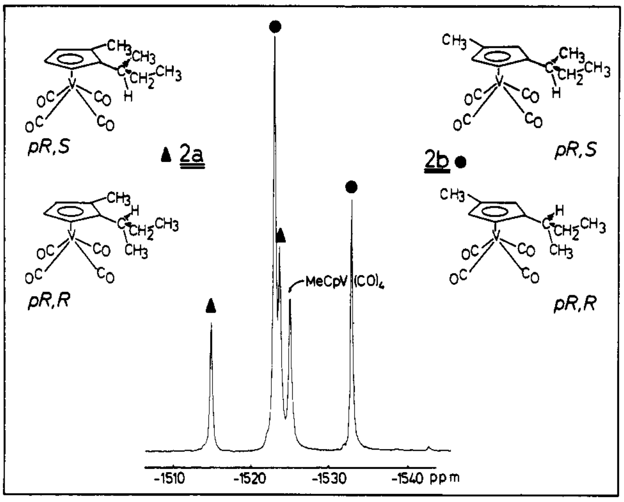
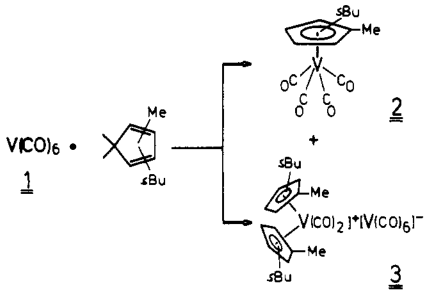
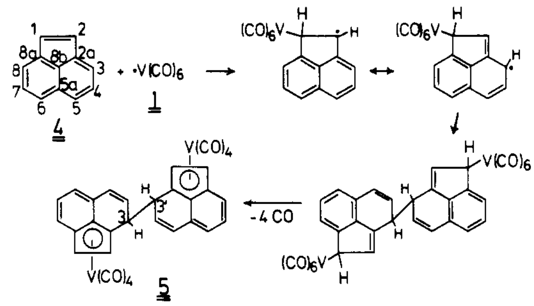


Figure 1. 94.6-MHz ^{51}V NMR spectrum of **2a** and **2b** in $CHCl_3/CDCl_3$ (1/1). δ(^{51}V) values relative to $C_5H_5V(CO)_4$ are as follows: (*pR,R*)-**2a**, +19; (*pR,S*)-**2a**, +10, (*pR,R*)-**2b**, +11; (*pR,S*)-**2b**, +1 ppm (δ[$C_5H_5V(CO)_4$] relative to the standard $VOCl_3$ is −1534 ppm at 298 K). The assignment of the signals has been carried out in view of enhanced deshielding of the vanadium nucleus as steric crowding in the coordination sphere increases.[1] The signal for $C_5H_4MeV(CO)_4$ is at +9 ppm.

Scheme I



Scheme II



Tentatively, we may assume that $\overline{\mathrm{Cp}}$H is attacked by 1 at the ring directly, as has been postulated for the primary step in the reaction between 1 and methylfulvene.[4] A radical intermediate is formed, which is stablized by

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(1) Rehder, D. *J. Magn. Reson.* **1980**, *38*, 419; *Bull. Magn. Reson.* **1982**, *4*, 33; *Magn. Reson. Rev.* **1984**, *9*, 125.

(2) 1 (500 mg, 2.3 mol) dissolved in 40 mL of highly purified *n*-hexane was treated with 405 mg (3.0 mmol) of C_5H_4(Me)*s*-Bu[17] and refluxed, under Ar atmosphere, for 3 h to yield a greenish orange solution containing 2 as the main product. Simultaneously formed 3 and small amounts of finely divided vanadium metal were filtered off. The filtrate was evaporated to dryness (vacuum, room temperature) and the residual orange oil chromatographed on silica gel[18] with hexane as eluant. 2 (630 mg, 70%) was recovered from the orange fraction by evaporation. During the whole procedure, direct sunlight has to be avoided, since 2 is light-sensitive. IR (cm^{-1}, *n*-hexane, ν(CO)): 2028, m, 1920 vs, 1890 sh (^{13}CO). MS (*m/e*, relative intensities in parentheses, selected peaks only): 2, 298 (32); 2 − 4CO, 186 (100) (degradation of the four CO groups occurs successively); $\overline{\mathrm{Cp}}$V(CO) − CH_3C_2H ($\overline{\mathrm{Cp}}$ = C_5H_3(Me)*s*-Bu), 172 (45); $\overline{\mathrm{Cp}}$V − CH_4, 170 (18); $\overline{\mathrm{Cp}}$V − C_2H_2, 160 (82); $\overline{\mathrm{Cp}}$V − CH_3C_2H, 146 (32).

(3) This reaction type has been employed by Herrmann et al. (Herrmann, W. A.; Kalcher, W. *Chem. Ber.* **1982**, *115*, 3886) for the preparation of $C_5Me_5V(CO)_4$. For other $\overline{\mathrm{Cp}}$V(CO)$_4$ see: Rehder, D.; Duch, A.; Hoch, M. *Inorg. Chem.* **1986**, *25*, 2907.

(4) Hoffmann, K.; Weiss, E. *J. Organomet. Chem.* **1977**, *131*, 273. Investigations carried out with C_5H_5D in our laboratory also support this mechanism (unpublished).

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Table I. Fractional Atomic Coordinates of the Non-Hydrogen Atoms[a]

atom	x/a	y/b	z/c
V	0.2045 (2)	0.8990 (2)	0.7236 (1)
C1*	−0.0074 (15)	0.9732 (12)	0.6521 (8)
C2*	0.3083 (13)	1.1295 (14)	0.6642 (8)
C3*	0.3461 (17)	1.0341 (13)	0.8446 (9)
C4*	0.0125 (18)	0.8911 (14)	0.8333 (8)
C2	0.3295 (13)	0.7529 (12)	0.5884 (8)
C1	0.4439 (13)	0.7568 (14)	0.6824 (8)
C8a	0.3419 (14)	0.6496 (13)	0.7578 (8)
C8b	0.1601 (12)	0.5896 (11)	0.7137 (7)
C2a	0.1499 (12)	0.6488 (11)	0.6090 (6)
C8	0.3736 (18)	0.5954 (17)	0.8632 (9)
C7	0.2375 (22)	0.4819 (17)	0.9115 (9)
C6	0.0565 (18)	0.4252 (15)	0.8648 (9)
C5a	0.0124 (16)	0.4787 (11)	0.7640 (8)
C5	−0.1669 (14)	0.4475 (13)	0.7099 (7)
C4	−0.1844 (13)	0.4985 (12)	0.6132 (8)
C3	−0.0224 (12)	0.5786 (11)	0.5406 (7)
O1*	−0.1307 (11)	1.0165 (10)	0.6091 (7)
O2*	0.3676 (11)	1.2619 (10)	0.6270 (6)
O3*	0.4402 (15)	1.1181 (12)	0.9076 (7)
O4*	−0.1066 (15)	0.8816 (13)	0.8939 (7)

[a] The atoms with an asterisk belong to the four carbonyls; for the numbering scheme see Figure 2 and Scheme II.

elimination of H_2 (and CO) to form a π complex. Support for this mechanism comes from the reaction of 1 with acenaphthylene (4),[5] where the radical intermediate (Scheme II) cannot be stabilized by H abstraction. Instead, a dimer is formed, the double half-sandwich 5 with acenaphthylene in the new bis(η^5) coordination. So far, the following coordination modes of 4 have been documented: 1,2-η^2 [in 4-CpCr(CO)NO,[6] 4-Mn(CO)$_2$Cp (Cp = η^5-C_5H_5),[7] and 4-Fe(CO)$_4$[8]]; 2a,3,4,5,5a,8b-η^6 [4-Cr(CO)$_3$[9]], and 1,2,2a,8a,8b-η^5 (5,5a,6-η^3) [4-Fe$_2$(CO)$_5$[10]]. The bis(1,2,2a,8a,8b-η^5) mode that we observe here is reminiscent of the related complexes of several transition metals with azulene (6), e.g. [6-Mo(Me)(CO)$_3$]$_2$,[11] [6-Mn(CO$_3$]$_2$,[12] and possibly also [6-V(CO)$_4$]$_2$.[13]

There are two centers and two planes of chirality in 5, which can give rise to a maximum number of four diastereomeric pairs of enantiomers plus two meso forms, namely, *pS,R,S,pR* (**5a**; corresponding with the exo–exo linkage of the two acenaphthylene moieties) and *pR,R,S,pS* (endo–endo). While, in solution, both meso forms (none of the enantomers, however) can be detected by ^{51}V NMR spectroscopy,[14] the crystal structure determination[15] of 5 (for the fractional coordinates of the non-hydrogen atoms see Table I) reveals the exo–exo complex **5a** (Figure 2), at least in the crystal that has been under investigation. The distance between vanadium and the ring plane (of the Cp unit) amounts to 193 pm which is the same or close to what we have found for CpV(CO)$_4$ and several of its derivatives substituted at the Cp ring and/or in the carbonyl ligand domain.[16] The acenaphthylene ring system is remarkably coplanar throughout, with a deviation for C3 of 20.3 pm

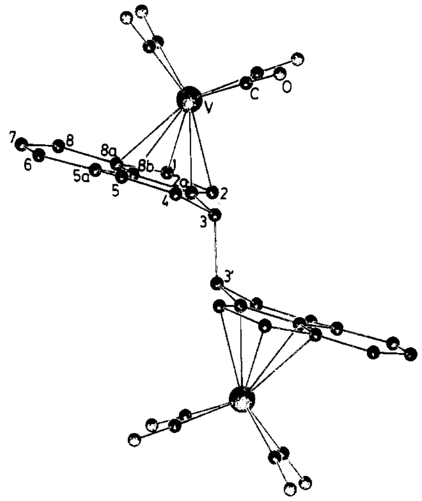

Figure 2. The molecular structure of **5a** in the crystal. Selected bond lengths (pm) and bond angles (deg) are as follows: mean V–CO, 194.7; mean C–O, 113.7; mean V–C–O, 177.1; V–plane-(C1,C2,C2a,C8b,C8a), 193.0; C1–C2, 142.3 (1.0); C1–C8a, 141.5 (1.0); C2–C2a, 141.7 (1.0); C2a–C8b, 142.6 (0.9); C8b–C8a, 140.9 (1.0; C2a–C3, 151.6 (1.0); C3–C4, 153.2 (1.1); C4–C5, 131.1 (0.9); C5–C5a, 143.4 (1.1); C5a–C6, 139.9 (1.1); C6–C7, 142.2 (1.3); C7–C8, 135.0 (1.2); C8–C8a, 144.2 (1.1); C3–C3′; 160.2 (1.4); C3–plane (1,2,2a,5a,6,7,8,8a,8b), −20.3; plane[(CO)$_4$]-plane-(1,2,2a,5a,6,7,8,8a,8b), 5.5; plane[(CO)$_4$]-plane(1,2,2a,8a,8b), 3.0.

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[5] 1 (700 mg, 3.2 mmol) and 630 mg (4.16 mmol) of 4, each dissolved in 25 mL of *n*-hexane, were combined and stirred for 24 h (room temperature). The orange precipitate of 5 was filtered off, combined with further product obtained during the concentration of the filtrate, and washed with three 5-mL portions of hexane. The product was then redissolved in 5 mL of THF, filtered, evaporated, and dried under high vacuum to yield 910 mg (90%) of orange **5a** + **5b**, mp 168 °C (dec). Sublimation at 120 °C and 0.01 Torr leads, with partial decomposition into acenaphthylene, vanadium, and CO, to small red needles of 5. Single crystals of **5a** in the form of thin, orange platelets form within 2 days in a hexane solution containing 1 and 4 in about one-third of the above concentration. IR (cm^{-1}, ν(CO)): 2030 s, 1945 sh (B_1), 1916 vs in toluene; 2028 m, 1914 s in CH_3CN. MS (for specification see ref 2): 5 − 8CO, 406 (0.5); $^1/_2$ **5**, 315 (5); $^1/_2$ **5** − 4CO, 203 (74) (all fragments formed by stepwise CO elimination have been observed); (acen)V − C_2H_2 (acen = $C_{12}H_8$), 177 (2.6); acen, 152 (100); acen − C_2H_2, 126 (6); the peak of the parent ion has not been detected.

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[13] Proposed structure in: Deganello, G. *Transition Metal Complexes of Cyclic Polyolefins*; Academic: New York, 1979; 122. Originally, the compound has been formulated as bis(dienyl) complex with a V–V bond (Priebe, E. Dissertation, München, 1962).

[14] In $CDCl_3$, there are two signals (**5a** and **5b**) at +187 and +178 ppm, respectively, relative to $C_5H_5V(CO)_4$, in the approximate intensity ratio 3/1.

[15] Crystal data: triclinic, $P\bar{1}$, a = 718.12 (0.27) pm, b = 751.83 (0.21) pm, c = 1260.04 (0.52) pm, α = 92.85 (0.03)°, β = 90.02 (0.03)°, γ = 99.80 (0.03)°, Z = 2 (one formula unit), V = 669.51 × 10^6 (pm)^3, ρ(calcd) = 1.5634 kg/L; μ = 6.92 cm^{-1}. Data were collected at room temperature on a Syntex P2$_1$ diffractometer using graphite-monochromator Mo K α. A total of 1928 reflections (2θ = 45°) were collected by using the $\theta 2\theta$ scanning technique. No emperical absorption correction was applied. A total of 1143 independent reflections with $|F_o| > 4\sigma(F_o)$ were used in the least-squares refinements. The structure was solved by use of the program systems SHELX-76 (Sheldrick, G. M. *Program for Crystal Structure Determination*; Cambridge, 1976) and SHELXS-86 (Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford 1985; p 185). All non-hydrogen atoms were refined anisotropically. The hydrogens were placed into calculated positions and included in the structure factor calculations, but not refined: R = 0.063, R_w = 0.046.

[16] CpV(CO)$_2$dppe (Cp = C_5H_5): Rehder, D.; Müller, I.; Kopf, J. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1013. CpV(CO)(triphos): von Deuten, K.; Rehder, D.; Roose, W. *J. Organomet. Chem.* **1981**, *214*, 71. CpV(CO)$_3$As$_2$Ph$_4$: Borowski, R.; Rehder, D.; von Deuten, K. *J. Organomet. Chem.* **1981**, *220*, 45 and unpublished results. For CpV(CO)$_4$ see also: Wilford, J. B.; Whitla, A.; Powell, H. M. *J. Organomet. Chem.* **1967**, *8*, 495.

[17] Freshly distilled C_5H_5Me dissolved in THF was treated, at 0 °C, with an equimolar amount of NaH and afterward with an equimolar amount of *s*-BuBr. After 1 h of refluxing, the solution was evaporated and the residue redissolved in ether and washed with H_2O. The etheric layer was dried with $MgSO_4$, the ether distilled off, and the remaining liquid distilled (138 °C, 10 Torr) to yield a mixture of 1,2- and 1,3-C_5H_4(Me)*s*-Bu.

[18] Kieselgel, Merck, 70–230 mesh ASTM. Before use, the silica gel was dried for 4 h under high vacuum (room temperature) and treated with N_2. Column dimensions: 2.5 × 15 cm.

from the indenyl plane. The distance C3–C3′ [160.2 (1.4) pm] is significantly longer than the "normal" C–C bond length between sp^3-hybridized carbon atoms. It is comparable, however, to what has been found in the bis(azulenyl) complexes $[6\text{-}Mn(CO)_3]_2$ and $[6\text{-}Mo(Me)(CO)_3]_2$ (158 pm).[12]

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Registry No. 1, 14024-00-1; (*pR,R*)-**2a**, 111349-33-8; (*pR,S*)-**2a**, 111464-95-0; (*pR,R*)-**2b**, 111349-34-9; (*pR,S*)-**2b**, 111465-82-8; **3a**, 111349-36-1; **3b**, 111349-38-3; **5a**, 111464-96-1; **5b**, 111349-39-4; C_5H_5Me, 26519-91-5; *s*-BuBr, 78-76-2; 1,2-C_5H_4(Me)-*s*-Bu, 111324-78-8; 1,3-C_5H_4(Me)-*s*-Bu, 111378-83-7.

Supplementary Material Available: Listings of refined atomic coordinates and anisotropic temperature factors, bond lengths, bond angles, and best planes and a numbering scheme (8 pages); a listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

Evidence for C–O Bond Formation, Aldehyde Decarbonylation, and Dimerization by Reaction of Formaldehyde and Acetaldehyde with *trans*-ROIr(CO)(PPh$_3$)$_2$

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Summary: The reaction of formaldehyde and acetaldehyde with *trans*-ROIr(CO)(PPh$_3$)$_2$ (R = Me, *i*-Pr, *n*-Pr, *t*-Bu) leads to formation of esters ROC(O)R′ (R′ = H or Me) by formation of a carbon–oxygen bond between the alkoxide and the acyl from the aldehyde and to catalytic production of the ester R′CH$_2$C(O)OR′ in a Tischenko reaction.

Reactions of aldehydes form the basis for many organic syntheses.[1] Reactions of aldehydes with metal complexes have been observed with a range of products formed.[2-10] Aldehydes react with metal bases in aldol condensation reactions, with strong bases in Cannizzaro reactions, and with aluminum alkoxides in Tischenko reactions.[11,12] The Tischenko reaction is an interesting dimerization that occurs by disproportionation of the aldehyde

$$2RC(O)H \xrightarrow{\text{cat.}} RCH_2OC(O)R$$

and may formally be considered as addition of a C–H bond to the carbon–oxygen double bond. This reaction is most effectively catalyzed by aluminum alkoxides[11-13] but can also be effected by transition-metal complexes.[14,15] As part of our continuing investigation of the interaction of organic molecules with *trans*-ROIr(CO)(PPh$_3$)$_2$,[16-23] we now communicate our preliminary observations on the reactions of formaldehyde and acetaldehyde with iridium alkoxides. These reactions lead to two separate paths, one involving Tischenko reactions and the other involving oxidative addition of the C–H bond to the iridium.

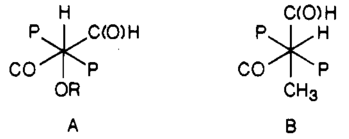
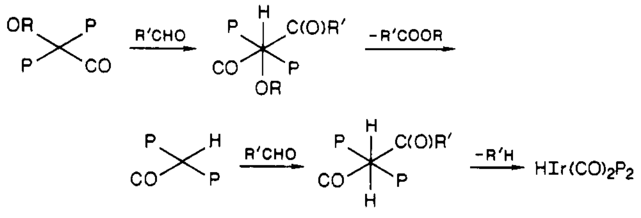


Figure 1. Suggested geometries for the formaldehyde oxidative addition to *trans*-ROIr(CO)(PPh$_3$)$_2$ (A) and *trans*-MeIr(CO)(PPh$_3$)$_2$ (B).

Scheme I[a]



[a] Abbreviations: P = PPh$_3$; R = Me, *n*-Pr, *i*-Pr, *t*-Bu; R′ = H, Me. The scheme is suggested for carbon–oxygen bond formation in reaction of aldehydes with *trans*-ROIr(CO)(PPh$_3$)$_2$. We cannot, at this time, rule out initial insertion of aldehyde into the Ir–OR bond followed by β-elimination.

Reactions of *trans*-ROIr(CO)(PPh$_3$)$_2$ (R = Me, *i*-Pr, *n*-Pr, or *t*-Bu)[24] with CH_2O and of *trans*-ROIr(CO)(PPh$_3$)$_2$ (R = Me) with CH_3CHO lead to catalytic production of Tischenko products, R′CH$_2$OC(O)R′, and to production of oxidative-addition, reductive-elimination products, R′C(O)OR, where R′ = Me or H, at ambient conditions over a period of several days.[25] When reaction ceases, the

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[24] Prepared as previously described.[17,18]