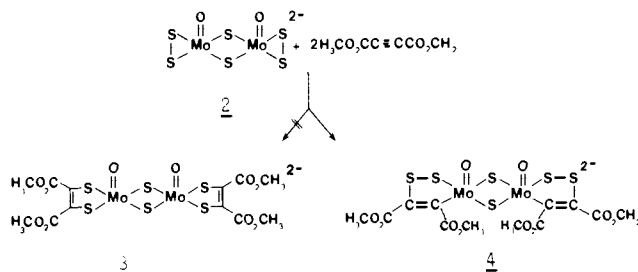addition to that at the 1,2-ethanedithiolate ligand. We thus turned to the well-known anion $[Mo_2O_2(\mu\text{-}S)_2(S_2)_2]^{2-}$ (**2**),[1b] where we expected that addition of DMAC would occur only at the terminal S_2^{2-} ligands to yield the bis-1,2-dithiolene complex (**2 → 3**).

Addition of 2 equiv of DMAC to a concentrated CH_3CN solution of $[N(C_2H_5)_4]_2[Mo_2O_2(\mu\text{-}S)_2(S_2)_2]$ at room temperature leads quickly to precipitation of an air-stable canary-yellow microcrystalline product.[11] Elemental analysis[12] indicates the formulation $[N(C_2H_5)_4]_2[Mo_2O_2(\mu\text{-}S)_2(S_2)_2\cdot2DMAC]$. However, while spectroscopic information[13] suggests retention of the $Mo_2O_2S_2^{2+}$ core and involvement of the S–S group, it requires an asymmetric environment for the acetylene-derived fragment. A single-crystal X-ray diffraction study was carried out to unambiguously determine the structure.

Single crystals were grown by slow vapor diffusion of 2-propanol into an acetonitrile solution of $[N(C_2H_5)_4]_2[Mo_2O_2(\mu\text{-}S)_2(S_2)_2\cdot2DMAC]$, and a full three-dimensional X-ray diffraction study was carried out.[14] The crystal contains ordered $Mo_2O_2(\mu\text{-}S)_2[S_2C_2(CO_2CH_3)_2]_2^{2-}$ dianions **4** as illustrated in Figure 1, along with disordered tetraethylammonium cations.[15] The source of the ligand asymmetry indicated by the spectroscopy is immediately clear and quite surprising: the acetylenes have inserted into Mo–S bonds of the terminal disulfides (rather than into S–S bonds) to form novel five-membered metalla-2,3-dithiacyclopent-4-ene rings. The dimensions of the five-membered rings are consistent with the presence of Mo—C_1, Mo—S_3, S_3–S_4, and C_2—S_4 single bonds and a C_1=C_2 double bond in an "vinyl disulfide" ligand. The "vinyl disulfide" ligand is very nearly planar (maximum deviation of 0.05 Å for a plane containing C_1, C_2, S_3, and S_4). The Mo atom lies out of this plane by 0.47 Å. The coordination geometry about each Mo is roughly square pyramidal with terminal oxo at the apex. The dimensions of the $Mo_2O_2S_2^{2+}$ core are little changed from those in the starting $[Mo_2O_2(\mu\text{-}S)_2(S_2)_2]^{2-}$.[16] The MoS_1S_2–$Mo'S_1S_2$ dihedral angle of 146.7° is slightly more acute than the average of 150–160° for known $Mo_2O_2S_2^{2+}$ core complexes.[1b]

Insertions of alkynes into transition-metal hydride[17] and carbon[18,19] bonds to form vinyl complexes are well-known and one

example has been reported of a reaction that may involve alkyne insertion into a Ni–P bond.[20] Although analogous insertions into transition-metal–sulfur bonds have also been claimed,[21] to our knowledge **4** is the first structurally characterized product of such an insertion. The factors that lead to such insertion rather than 1,2-dithiolene formation or direct π-coordination to molybdenum are not yet understood.[22] It seems likely that frontier molecular orbitals of molybdenum–sulfur complexes exhibit significant metal and sulfur character. The reactions of such complexes may involve coordinatively unsaturated sites on the metal,[8a–d] direct reactions with S ligands,[7,8e,f] or, as we have demonstrated here for the first time, reaction at a multicenter metal–sulfur site leading to insertion of a molecule into a metal–sulfur bond. Further systematic reactivity studies combined with theoretical treatments are required to fully understand these systems. Such work is in progress.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths and bond angles, structure factors, and perspective drawings of TEA⁺ cations (21 pages). Ordering information is given on any current masthead page.

(20) Lindner, E.; Bouachir, F.; Hiller, W. *J. Organomet. Chem.* **1981**, *210*, C37.

(21) Davidson, J. L.; Sharp, D. W. A. *Chem. Soc., Dalton Trans.* **1975**, 2283.

(22) For example, the reaction of MoS_9^{2-} with DMAC produces a Kelly-green product, which has recently been characterized in an X-ray study by Coucouvanis and co-workers[23] as the tris(1,2-dithiolene) complex. Thus, even in simple molybdenum thioanions, different modes of alkyne addition occur.

(23) Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1983**, *105*, 139.

Novel Approach to Vicinal Stereocontrol during Carbon–Carbon Bond Formation. Stereocontrolled Synthesis of (±)-*threo*-Juvabione

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The establishment of defined, vicinal stereorelationships in the construction of organic molecules is a central requirement for efficient synthesis of many structurally complex substances. An approach involving formation of the carbon–carbon bond linking two asymmetric centers can often provide a useful solution to the problem, particularly in acyclic systems. Schemes of this type (Scheme I) frequently involve bond formation between trigonal carbons (route a). The striking developments in stereocontrolled aldol reactions[1] provide testimony to the utility of this approach. An alternative to this strategy involves bond formation between a trigonal and *nontrigonal* carbon atom[2] (shown for a tetrahedral

(11) Yield on the basis of the formula $[N(C_2H_5)_4]_2Mo_2O_2(\mu\text{-}S)_2(S_2C_2\text{-}(CO_2CH_3)_2)_2$ is typically 60–65%.

(12) Anal. Calcd for $C_{28}H_{52}O_{10}S_6N_2Mo_2$: C, 35.00; H, 5.45; N, 2.92; S, 20.02. Found: C, 34.62; H, 5.31; N, 2.89; S, 19.84.

(13) Infrared (KBr) $\nu_{Mo=O}$ 947, $\nu_{Mo-S-Mo}$ 473; ν_{S-S} 520 cm⁻¹ in starting material is gone; ¹H NMR (Me₂SO-*d₆*) δ 3.77 (s, 6, ester CH₃), 3.72 (s, 6, ester CH₃), 3.13 (q, 16, cation CH₂), 1.11 (t, 24, cation CH₃); ¹³C (Me₂SO-*d₆*) δ 177.4, 176.6, 161.7, 149.3, 52.18, 51.85, 51.42, 51.31, 51.15, 50.55, 6.89.

(14) Crystal data: space group $P_{nma}\text{-}D_{2h}^{16}$ (No. 62) with $a = 18.314$ (5) Å, $b = 25.358$ (6) Å, $c = 8.916$ (2) Å, $V = 4141$ Å³, $Z = 4$. The structure was solved by conventional heavy-atom methods, difference Fourier synthesis and full-matrix least-squares refinement. $R_F = 0.048$, $R_{wF} = 0.057$ for 2276 independent diffracted intensities ($I > 3.0\sigma(I)$) with 3° < 2θ < 55° (Mo Kα radiation). Anisotropic thermal parameters were employed for all 31 independent non-hydrogen atoms.

(15) Perspective drawings of the two independent tetraethylammonium cations are included in the supplementary material. Both cations, though disordered, were fully characterized.
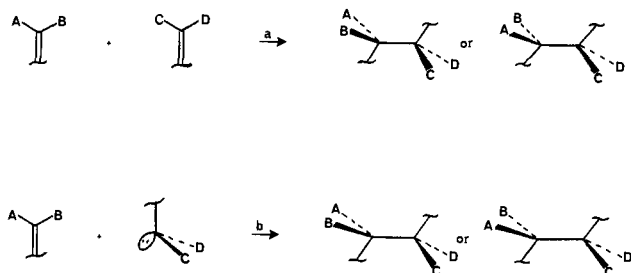
(16) For the $Mo_2O_2S_2^{2+}$ core[1b] in $[N(C_2H_5)_4]_2Mo_2O_2(\mu\text{-}S)_2(S_2)_2$, Mo=O is 1.67 Å, Mo—S$_{bridge}$ average 2.324 Å, Mo—Mo is 2.825 Å.

(17) Clark, H. C.; Milne, C. R. *J. Organomet. Chem.* **1978**, *161*, 51 and references cited therein.

(18) (a) Davidson, J. L.; Green, M.; Sharp, D. W. A.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1974**, 706. (b) Bottrill, M.; Green, M. *J. Am. Chem. Soc.* **1977**, *99*, 5795.

(19) (a) Tremont, S. J.; Bergman, R. G. *J. Organomet. Chem.* **1977**, *140*, C12 and references cited therein. (b) Clark, H. C.; Milne, C. R. C.; Wong, C. S. *Ibid.* **1977**, *136*, 265 and references cited therein.

*Address correspondence to this author at Syntex Research, 3401 Hillview Avenue, Palo Alto, CA 94304.

(1) For some recent examples see: (a) Masamune, S.; Kaiho, T.; Garvey, D. S. *J. Am. Chem. Soc.* **1982**, *104*, 5521. (b) Masamune, S.; Ellingboe, J. W.; Choy, W. *Ibid.* **1982**, *104*, 5526. (c) Evans, D. A.; Bartoli, J.; Sih, T. *Ibid.* **1981**, *103*, 2127. (d) Heathcock, C. H.; Pirrung, M. C.; Montgomery, S. H.; Lampe, J. *Tetrahedron* **1981**, *37*, 4087. (e) Meyers, A. I.; Yamamoto, Y. *J. Am. Chem. Soc.* **1981**, *103*, 4278. (f) Noyori, R.; Nishida, I.; Sahata, J. *Ibid.* **1981**, *103*, 2106.

(2) For a related case in which the site of nontrigonal asymmetry is remote from the site of bond formation see: (a) Kluge, A. F.; Untch, K. G.; Fried, J. H. *J. Am. Chem. Soc.* **1972**, *94*, 9256. (b) Miller, J. G.; Kurz, W.; Untch, K. G.; Stork, G. *Ibid.* **1974**, *96*, 6774. (c) Stork, G.; Takahashi, T. *Ibid.* **1977**, *99*, 1275. (d) Luthy, C.; Konstantin, P.; Untch, K. G. *Ibid.* **1978**, *100*, 6211. (e) Takahashi, T.; Naito, Y.; Tsuji, J. *Ibid.* **1978**, *103*, 5261.

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Communications to the Editor

Scheme I

carbanion in route b). In an attempt to determine the potential of the trigonal/nontrigonal case for stereocontrolled bond formation, we have examined a system involving organocopper addition (nontrigonal component) to an enone (trigonal component). We now report the results of this preliminary study: *an appropriately chosen nontrigonal nucleophile can undergo conjugate addition to an enone with considerable stereocontrol.* This observation constitutes the first reported example of this type of diastereoselection in conjugate addition reactions.[3] An illustration of the utility of this methodology is given in the first stereocontrolled synthesis of (±)-*threo*-juvabione[4] (**11**).

Our choice for the nontrigonal component was the known carbanion **1**. This substance, first generated by Corey and Ulrich[5]
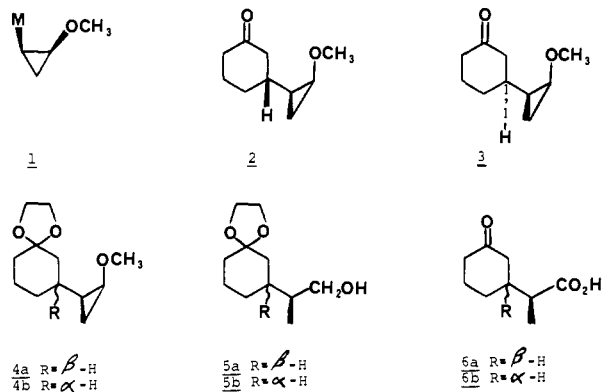
as the organolithium species, is readily available and well-behaved under conditions suitable for the study. Adducts derived from **1** and enones can be further transformed for the purpose of structure proof or use as synthetic intermediates by electrophilic cleavage of the cyclopropane ring.[6]

Numerous experiments revealed that reagents could be produced and reacted with cyclohexenone to yield **2** and **3** (mp 39–40 °C). Diastereomer ratios were determined by analyses of the total conjugate addition product (obtained by filtration of the crude reaction mixture through silica gel with 10:1 hexane/EtOAc) by capillary GC or semipreparative HPLC. The ratios obtained in this manner did not differ significantly from the ratios apparent in the ¹H NMR of the crude product (OCH₃). The results are summarized in Table I. Structures for the difficultly separable ketones **2** and **3** could not be assigned by NMR. Structure proof thus rested on conversion to a known substance.

For preparative purposes, the crude conjugate addition product was distilled (bp 64–65 °C (0.25 torr)), ketalized (2-methyl-2-

Table I. Representative Product Compositions

cuprate reagent[a]	isolated yield,[b] %	diastereomer ratio (2:3)
R₂CuLi/Et₂O/Me₂S	50	ca. 3:1[d]
CH₃O(CH₃)₂C-C₂CuR/Et₂O/THF	14	4.23:1[c]
t-C₄H₉C₂CuR/Et₂O	45	3.10:1[c]
PhSCuR/Et₂O	64	4.01:1[c]
C₃H₇C₂CuR/Et₂O/(Me₂N)₃P	52	5.46:1[c]
Bu₃PCuR/Et₂O	77	4-5:1[d]
Bu₃PCuR/Et₂O/1 equiv Bu₃P	65	5-6:1[d]

[a] All additions carried out by addition of cyclohexenone to the performed copper reagent at −78 °C. [b] Reported yields are for chromatographically purified products. [c] Obtained with a 10 M methyl silicone WCOT silica capillary column at 70 °C on a gas chromatograph equipped with a flame ionization detector and a digital integrator. [d] Isolated ratios obtained by separation of the diastereomers on a Whatman Partsil M9 column eluted with 10:1 petroleum ether-ethyl acetate.

Scheme II
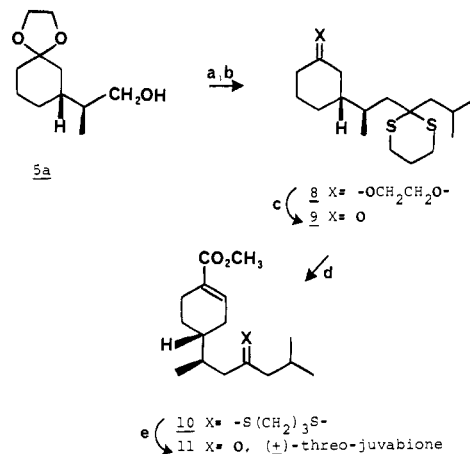
[a] MsCl, 1.1 equiv, Et₃N, 1.1 equiv, CH₂Cl₂, then treat with NaI (excess) in acetone, 50 °C, 24 h, 86%. [b] 2 equiv of lithio-2-(2-methylpropyl)-1,3-dithiane, −78 to 0 °C, 0.75 h, 89%. [c] 10% aqueous HCl in THF, RT, 24 h, quantitative yield. [d] NaH, (MeO)₂CO, then NaBH₄, EtOH followed by MsCl, Et₃N, CH₂Cl₂, and treatment with NaOMe in C₆H₆—see ref 8. [e] AgNO₃, MeOH, H₂O, 90%.

ethyl-1,3-dioxolane, 10 equiv, TsOH, 100%), and separated by MPLC[7] to afford dioxolanes **4**. Each isomer was separately converted to acids **6a** and **6b** (mp 76–77 °C (lit. mp 76 °C,[8a] 77–78 °C[8b])) via the alcohols **5** (Hg(OAc)₂, 1.2 equiv, RT, 4:1 THF/H₂O, 7 h then NaBH₄, 0 °C, 94% yield at 64% conversion followed by Jones oxidation in acetone). Spectroscopic comparison (500-MHz ¹H NMR) with an authentic sample[9] of **6b** unambiguously defined the structure of the minor acid, thus establishing structure **2** for the major conjugate addition product.

The synthesis of (±)-*threo*-juvabione was accomplished as shown in Scheme II. Conversion of **2a** into **8** via the derived iodide **7** followed by dioxolane hydrolysis yielded **9**, which, after further elaboration using the Ficini–Evans protocol[8] produced **10**. Dithiane hydrolysis gave (±)-*threo*-juvabione (**11**) identical with naturally derived material[11] by all the usual criteria (IR, ¹H NMR, ¹³C NMR, EI MS, and HPLC).

These results clearly illustrate the utility of this type of conjugate addition to the solution of a long-standing problem in organic

(3) Corey and Ulrich first described the diastereoselection observed in the 1,2-addition of **1** (M = Li) to aldehydes (ref 5).

(4) In this paper we adopt the convention suggested by Evans (ref 8b) for naming the juvabione isomers. For references to *threo*-juvabione see: (a) Rogers, I. H.; Manville, J. F.; Sahota, T. *Can. J. Chem.* **1974**, *52*, 1192. (b) Manville, J. F. *Ibid.* **1975**, *53*, 1579; (c) *Ibid.* **1976**, *54*, 2365.

(5) Corey, E. J.; Ulrich, P. *Tetrahedron Lett.* **1975**, 3685.

(6) (a) De Puy, C. H. *Forschr. Chem. Forsch.* **1973**, *40*, 73. (b) De Boer, A.; De Puy, C. H. *J. Am. Chem. Soc.* **1970**, *92*, 4008. (c) De Puy, C. H.; McGick, R. H. *Ibid.* **1973**, *95*, 2366. As an alternative to the scheme illustrated, formation of a carbon–carbon bond at the mercury-bearing carbon could proceed directly from the mercurial. See: Giese, B.; Zwick, H. *Chem. Ber.* **1982**, *115*, 2526.

(7) Meyers, A. I.; Slade, J.; Smith, R. K.; Mihelich, E. D. *J. Org. Chem.* **1979**, *44*, 2247.

(8) (a) Ficini, J.; Touzin, A. M. *Tetrahedron Lett.* **1972**, 2093, 2097. (b) Evans, D. A.; Nelson, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 774.

(9) Spectra of **6a**, **6b**, and an authentic example of **6b**[8b] were obtained at the Regional NMR Facility at the California Institute of Technology. We thank Professor Evans for his assistance in obtaining these spectra.

(10) Roberts, R. M.; Cheng, Ch.-Ch. *J. Org. Chem.* **1958**, *23*, 983.

(11) Kindly provided by J. F. Manville of the Canadian Forest Service.

synthesis[12] and point the way for further development using other asymmetric, nontrigonal carbon nucleophiles.[13] Results of further studies will be described in due course.

Supplementary Material Available: A listing of purification and characterization data for all compounds (4 pages). Ordering information is given on any current masthead page.

(12) See (a) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 3435. (b) Trost, B. M.; Taber, D. F.; Alpen, J. B. *Tetrahedron Lett.* **1976**, 3857. (c) Ficini, J.; d'Angelo, J.; Noire, J. *J. Am. Chem. Soc.* **1974**, *96*, 1213. See ref 8 and 2e for some recent approaches.

(13) (a) Still, W. C.; Sreekumar, C. *J. Am. Chem. Soc.* **1980**, *102*, 1201. (b) McGarvey, G. J.; Kimura, M. *J. Org. Chem.* **1982**, *47*, 5420.

The First Triple-Decker Sandwich with a Bridging Benzene Ring

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Until now triple- and tetra-decker sandwich complexes have only been prepared with five-[1] or eight-membered[2] carbocyclic or heterocyclic[3] groups or group 5 element rings (P$_3$, As$_3$,[4] or As$_5$[5]) as the bridging ligands. Considering that many examples of mononuclear complexes with η^6-bound arenes are known,[6] it is indeed surprising that no reports of multiple deckers containing bridging arenes have yet appeared in the literature.

We wish to report the preparation and characterization of the first examples of arene-bridged, binuclear transition-metal compounds with triple-decker sandwich structures. In these novel complexes, two (cyclopentadienyl)vanadium moieties are linked by benzene, toluene, *n*-propylbenzene, or mesitylene. They are formally unsaturated 26-electron complexes, and as such violate the "30- and 34-electron rule" put forward by Hoffmann et al. for triple-decker sandwiches.[7] The parent complex **1**, with benzene as the central fragment, was prepared by reaction of CpV(C$_3$H$_5$)$_2$[8]

(1) (a) Salzer, A.; Werner, H. *Inorg. Metal-Org. Chem.* **1972**, *2*, 239. (b) Werner, H., *Angew. Chem.* **1977**, *89*, 1.

(2) Geiger, W. E.; Moraczewski, I. *J. Am. Chem. Soc.* **1978**, *100*, 7429. Dobson, J. E.; Kolesnikov, S. P.; Skell, P. S. *Ibid.* **1978**, *100*, 999.

(3) Siebert, W. *Adv. Organomet. Chem.* **1980**, *18*, 301.

(4) Sacconi, L.; Di Vaira, M. *Angew. Chem.* **1982**, *94*, 338.

(5) Reingold, A. L.; Folly, M. I.; Sullivan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4727.

(6) Bleeke, J. R.; Muetterties, E. L.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

(7) Elian, M.; Hoffmann, R.; Lauher, J. W.; Summerville, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 3219.
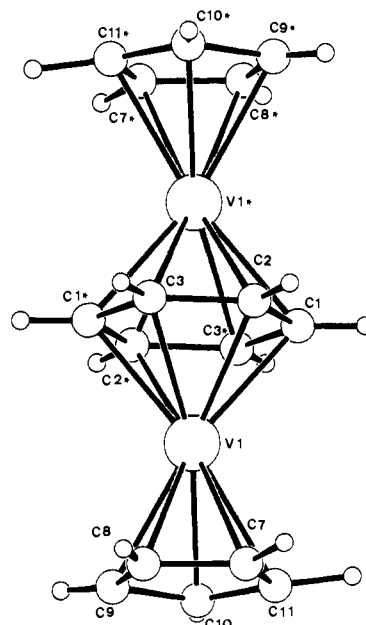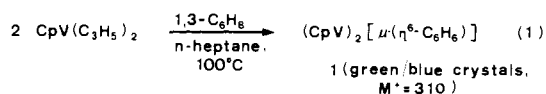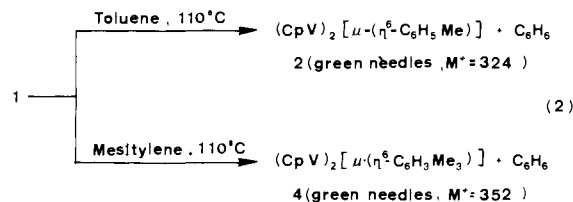
Figure 1. **1** crystallizes in the monoclinic space group $P2_1/n$ with Z = 2 and cell dimensions a = 6.068 (1) Å, b = 7.928 (1) Å, c = 13.821 (1) Å, β = 96.94 (1)°; center of inversion at the midpoint of the central benzene ring. R 0.051 (R_w 0.074) for 114 parameters and 2129 reflections (λ 0.71069, ϑ_{max} 30°) of which 1946 were considered observed (2σ).

with an excess of 1,3-cyclohexadiene in refluxing *n*-heptane (eq 1).

$$2 \ \text{CpV(C}_3\text{H}_5)_2 \ \xrightarrow[\substack{\text{n-heptane,} \\ 100°\text{C}}]{1,3\text{-C}_6\text{H}_8} \ (\text{CpV})_2[\mu\text{-}(\eta^6\text{-C}_6\text{H}_6)] \qquad (1)$$

1 (green/blue crystals, M$^+$ = 310)

Compound **1** was obtained in about 50% yield.[9] Hydrogen, propene, cyclohexene, 1,5-hexadiene, benzene, and *n*-propylbenzene are other products of the reaction. Two further organovanadium species were also isolated from the reaction mixture. They were identified by mass spectrometry as the *n*-propylbenzene analogue of **1**, (CpV)$_2$C$_6$H$_5$Pr (**3**), and the mononuclear complex CpV(C$_6$H$_5$Pr) (**5**). An attempt to isolate the parent compound, CpV(C$_6$H$_6$), from the reaction mixture of CpVCl$_3$, C$_3$H$_7$MgCl, and 1,3-cyclohexadiene has been unsuccessful.[10]

It is interesting to note that **1** readily undergoes arene exchange reactions with retention of the triple-decker sandwich structure. Thus **1** may be converted to the toluene or mesitylene analogues, **2** or **4**, respectively, according to eq 2.[11] In contrast to **1**, both

$$1 \ \begin{cases} \xrightarrow{\text{Toluene, 110°C}} (\text{CpV})_2[\mu\text{-}(\eta^6\text{-C}_6\text{H}_5\text{Me})] \cdot \text{C}_6\text{H}_6 \\ \qquad\qquad \text{2 (green needles, M}^+ = 324) \\ \\ \xrightarrow{\text{Mesitylene, 110°C}} (\text{CpV})_2[\mu\text{-}(\eta^6\text{C}_6\text{H}_3\text{Me}_3)] \cdot \text{C}_6\text{H}_6 \\ \qquad\qquad \text{4 (green needles, M}^+ = 352) \end{cases} \qquad (2)$$

of these new triple-deckers are highly soluble in ethers, aliphatic and aromatic hydrocarbon solvents.

Complexes **1–4** have been characterized by mass spectrometry. Parent ions were observed in all cases. In addition, satisfactory elemental analyses have been obtained for **1**, **2**, and **4**.

(8) (a) Wiskamp, V. Dissertation, Universität Bochum, **1981**. (b) Jonas, K.; Wiskamp, V. *Z. Naturforsch.*, submitted for publication.

(9) Toluene was found to be the most suitable solvent for recrystallization, in spite of the low solubility (ca. 8 g/L at 110 °C) and loss due to the exchange reaction with toluene (see eq 2).

(10) Goll, W.; Müller, J. *J. Organomet. Chem.* **1974**, *71*, 257.

(11) The formation of two further CpV organyls was observed. These were isolated as volatile (60 °C/10^{-4} mmHg) brown oils whose mass spectra corresponded to CpV(C$_6$H$_5$Me) and CpV(C$_6$H$_3$Me$_3$).

(12) Isolated yields were not optimized.