

would parallel rather than cross under the Ln(DHMP)²⁺ sequence between Sm and Lu.

2. Adding a second methyl group to the third carbon atom of our ligand (to give 2,3-dihydroxy-2,3-dimethylbutanoate) should enhance its affinity when it exhibits tridentate liganacy with lanthanons that are neither too large nor too small (Pr through Gd) but should further decrease the affinity of the bidentate ligand associated with smaller lanthanons (Dy–Lu) and yttrium. That is, the additional inductive effect of a second close-by –CH₃ group on the β-OH O atom should make DHDMB a better donor than DHMB when conditions are optimum for tridentate attachment, but its added bulk ought to cause the end of the anion to collide more frequently with a hydrated metal cation whenever the ligand binds only bidentately. The “club” effect of a terminal HO(CH₃)₂C– group should be similar to that encountered with the (CH₃)₃C– group of 2-hydroxy-2,3,3-trimethylbutanoate (HTMB), so that the formation constant sequences from Dy through Lu for Ln-(DHDMB)²⁺ and Ln(HTMB)²⁺ species should nearly coincide, as do those for Ln(DHMB)²⁺ and Ln(HDMB)²⁺.

3. If the favorable positioning of the β-OH H atom in DHMB for hydrogen bonding to a carboxyl O is the reason for the increase in the acid ionization from DHMP to DHMB, then this trend may reverse itself with DHDMB, due to an attenuated ability of the latter ligand to rotate (or twist) about the 2–3 bond in the carbon chain. The acid ionization in the case of DHDMB might conceivably drop to a value coincident with that of 2-hydroxy-2,3,3-trimethylbutanoic acid, which has been determined in this laboratory to be about 1.14×10^{-4} at 25° and $I = 0.10$ (NaClO₄). This prediction, however, is subject to some reservations (in the event that the opposite inductive effects of the HO– and CH₃– are capable of being transmitted along a three-carbon chain to the carboxyl O atom). Certainly, the ionization constant of DHDMB will be found to be less than that of DHMP (2.65×10^{-4} at 25° and $I = 0.100$) but not less than that of HTMB.

Registry No. DHMP, 21620-60-0; DHMB, 40634-99-9; La, 7439-91-0; Ce, 7440-45-1; Pr, 7440-10-0; Nd, 7440-00-8; Sm,

7440-19-9; Eu, 7440-53-1; Gd, 7440-54-2; Tb, 7440-27-9; Dy, 7429-91-6; Ho, 7440-60-0; Er, 7440-52-0; Tm, 7440-30-4; Yb, 7440-64-4; Lu, 7439-94-3; Y, 7440-65-5.

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Metal Atom Reactions with Fluorocarbons. VI. Complexes of Halogenated Benzenes with Vanadium(0) and Chromium(0). Effects of Strongly Electron-Withdrawing Substituents, Particularly Trifluoromethyl Groups

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Vapors of vanadium and chromium were cocondensed with arene substrates to yield bis(arene)vanadium(0) and -chromium(0) complexes. A number of halogenated arenes were studied as ligands, and trifluoromethyl substitution enhanced the air stability of the complexes considerably. The presence of two trifluoromethyl groups (1,3- or 1,4-bis(trifluoromethyl)benzene) caused the preparation of the complexes to fail in the case of vanadium, but in the case of chromium extremely air- and temperature-stable complexes were formed in good yields. However, infrared studies suggested that the ring-metal bonding is weaker in bis(1,4-bis(trifluoromethyl)benzene)chromium(0) than in bis(benzene)chromium(0).

Introduction

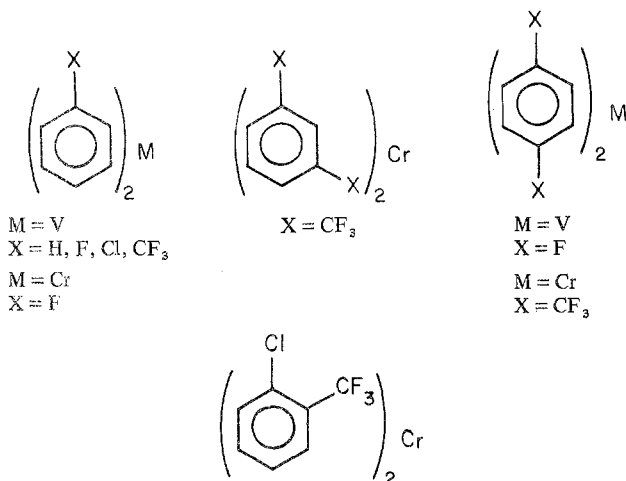
The technique of cocondensing free metal atoms with organic substrates at low temperature has proven to be a viable method of synthesizing many new as well as known organometallic complexes.¹⁻⁶ A considerable amount of effort in this area has been on the use of chromium atoms for the synthesis of bis(arene)chromium(0) complexes. Timms⁷ was the first to report the production of bis(benzene)chromium(0) itself using the metal atom technique, and Skell,³ Timms,^{2b} Lagowski,⁸

and their coworkers have all reported on the use of chromium atoms for synthesis of a number of substituted sandwich complexes. Recently, molybdenum, tungsten,^{3b} and titanium⁵ atoms have also been employed for synthesis of arene π complexes. We have also been working in this area for quite some time^{9,10} and have been mainly concerned with polyhalogenated benzene complexes with chromium as well as vanadium. In this paper we report on the synthesis, properties, and spectra of a series of bis(arene) complexes with vanadium

and chromium. Substitutions of chlorine, fluorine, and especially trifluoromethyl groups have very interesting and useful effects on these materials.

Results and Discussion

Vanadium. Vanadium vapor, generated by vaporization from a resistively heated tungsten boat (details of apparatus and techniques have been described^{1,2,10,11}), was cocondensed at -196° with >15-fold excesses of arene substrates. Red-brown matrices were usually formed. After warm-up the products were isolated under inert atmosphere and purified by sublimation. The bis(arene)vanadium(0) complexes exhibited very characteristic and readily interpretable mass spectra as well as characteristic infrared spectra (*cf.* Experimental Section). Shown in the structures are the complexes



that were prepared. Bis(benzene)vanadium(0) was formed in small yield, based on metal vaporized, whereas higher yields were obtained with fluoro-, chloro-, and trifluoromethylbenzene. Then, when bis-substituted arenes were employed, only a small yield of bis(1,4-difluorobenzene)vanadium(0) was found and no products at all were formed with 1,3- and 1,4-bis(trifluoromethyl)benzenes. In the case of benzene itself, the reason for the poor yield is not readily apparent. However, it does appear from these data that the presence of two strongly electron-withdrawing substituents (F or CF_3) definitely disfavored complex formation using the metal atom technique. Monosubstitution seemed to help, however.

These halogenated sandwich complexes showed increased air stabilities over bis(benzene)vanadium itself. In solution they were quite air sensitive, but in crystal form, air could be tolerated for at least several minutes.

Chromium. Chromium atoms codeposited with the arene substrates indicated usually yielded yellow-brown matrices. Better yields of complexes were obtained with chromium than with vanadium, and both 1,3-, and 1,4-bis(trifluoromethyl)benzenes as well as *o*-chlorobenzotrifluoride gave respectable yields of sandwich compounds. A striking thing about these bis(trifluoromethyl)-substituted complexes is their extremely good air stability and thermal stability. As evidence of this bis(1,3-bis(trifluoromethyl)benzene)chromium(0) could be boiled (200°) in air with only slow decomposition. Similar air stabilities were found for the 1,4-bis(trifluoromethyl)benzene and *o*-chlorobenzotrifluoride complexes. These materials are indefinitely stable at room temperature in air while the benzotrifluoride complex very slowly decomposed over a several-week period. However, in halogenated solvents such as CCl_4 , CHCl_3 , and CH_2Cl_2 all of these complexes decomposed fairly rapidly.

We attempted to make direct comparisons of some of the important infrared bands in bis(benzene)chromium(0) with bands in the substituted complexes. However, generally the

spectra obtained were quite complex, and only in the case of bis(1,4-bis(trifluoromethyl)benzene)chromium(0) do we feel confident of a few band assignments. Thus, we looked at the aryl in-plane stretching vibration region. Yamoda, Nakamura, and Tsuchida¹² reported that the 1500-cm^{-1} band in benzene shifts to 1428-cm^{-1} upon complexation with chromium ($\Delta\nu_{\text{C}=\text{C}} = 72\text{-cm}^{-1}$). In 1,4-bis(trifluoromethyl)benzene the analogous band at 1529-cm^{-1} shifts to 1480-cm^{-1} upon complexation ($\Delta\nu_{\text{C}=\text{C}} = 49\text{-cm}^{-1}$). Thus, there is less C=C bond weakening upon complexation in the 1,4-(CF_3)₂ case, which would in turn suggest a slightly weaker ring-metal bond in the 1,4-(CF_3)₂ case than in bis(benzene)chromium(0).

The unusual air stability of these complexes possessing highly electronegative substituents must be a kinetic effect. This increased air stability might have been predicted since the first step in the facile oxidative decomposition of bis(benzene)chromium(0) and analogous complexes possessing electron-donating substituents is the one-electron oxidation of chromium yielding a Cr^+ complex.^{2b,13} This process would be disfavored by more strongly electron-withdrawing complexed arenes.

Currently we are doing X-ray crystallographic studies (with L. Radonovich) on some of these substituted sandwich complexes in an attempt to learn more about unusual bonding effects. Also, one-electron polarographic oxidations are also being studied.

Trifluoromethyl substitution has a very favorable effect on the air stability of these vanadium and chromium complexes while not adversely affecting their thermal stability. In the case of fluorine or chlorine substitution, air stability is also enhanced, but not as greatly.^{3,14} Also, in monofluoro and polyfluoro cases explosive character has been encountered.^{9,14} In fact, when more than two fluorines are attached to the arene ligand, only unstable, very explosive chromium complexes are obtained.¹⁴ Apparently the aryl fluorines are quite labile, and on decomposition Cr-F (or V-F) bonds are formed in a very exothermic process. (Workers should be wary of this possible behavior in any organohalogenated π complexes of this type.) However, in the case of trifluoromethyl substitution, no explosive character has ever been encountered with the complexes in our hands.

Experimental Section

Apparatus. Our metal atom reactors are based on general designs already published by Skell¹¹ and Timms.² Details of our simplified system will soon be illustrated in print.^{1,10} Kontes-Martin Glass Co. now markets a reactor based on our design in combination with that of Timms.

Identification of Compounds. Bis(arene) sandwich complexes are readily identified by their characteristic mass spectra,^{2b,3,5,16a} and the compounds reported herein are no exceptions. Also, characteristic infrared bands are very helpful.^{5,16b} In the chromium series nmr analysis was obtainable. Elemental analyses were done as checks in a number of cases. However, the volatility, air sensitivity, and rapid M-X bond-forming process on heating caused poor reproducibility in analyses. In the vanadium series nmr spectra were not obtainable, of course, because of the paramagnetism of these materials.¹⁵

Typical Preparation of a Bis(arene) Complex. Bis(benzotrifluoride)vanadium(0). Vanadium was vaporized from a tungsten boat (Mathis S16, 0.005 w) at 2.5 V and 300 A. Simultaneously benzotrifluoride vapor was codeposited with the vanadium vapor on the liquid nitrogen cooled walls of the glass reactor. Codeposition continued for 10 min (35.4 mg, 0.70 mg-atom of vanadium; 10 ml benzotrifluoride). After completion of the reaction the cold matrix was red-black. It was allowed to warm slowly to room temperature and then pressurized with argon. With argon flushing, the solution was taken out by syringe and transferred to a sublimator. The excess ligand was slowly pumped off, and then the complex was sublimed to yield 51.2 mg (22%) of bis(benzotrifluoride)vanadium(0).

Modifications of the above procedure were employed when desirable or necessary. For example, the reactor could be disassembled in an argon-filled glove bag and product removed. Also, the substrate could

be pumped off, hexane vaporized in, and the complex taken out in hexane solution. Finally, when the complexes had sufficient vapor pressure to be sublimed directly from the reactor into a removable vacuum trap, this was done, *i.e.*, for bis(1,4-difluorobenzene)vanadium(0).

Physical Properties, Yields, and Spectra of Compounds. Bis(benzene)vanadium(0) [(C₆H₆)₂V]. The compound is dark red and very air sensitive and decomposes thermally at >300°^{13,16} (2% yield based on vanadium).

Bis(fluorobenzene)vanadium(0) [(C₆H₅F)₂V]. The compound is dark red (13% yield) and air sensitive and sublimes at 50–70° (<1μ); mass spectrum at 24 eV M (16), C₆H₅V (12), C₆H₅F (100), VHF (28), VF (15), V (4), V³⁺ (26); far ir in hexane in polyethylene (cm⁻¹) 444 s, 475 m; ir in hexane in KBr cell (cm⁻¹) 620 w, 685 m, 742 s, 752 s, 795 s, 808 s, 895 w, 974 m, 1020 m, 1067 w, 1105 w, 1155 w, 1200 s, 1225 s, 1235 s, 1263 s, 1505 s, 1600 s, 3080 w.

Bis(chlorobenzene)vanadium(0) [(C₆H₅Cl)₂V]. This material is orange-red (7% yield) and moderately air sensitive and sublimes at 50–60° (<1μ): mass spectrum at 24 eV M (24), M - Cl (8), C₆H₅ClV (5), C₆H₅ClV (30), C₆H₄V (36), C₆H₅Cl (100), C₁₂H₁₀ (63), C₆H₅ (40), VCl (6), V (9); far ir in hexane in polyethylene (cm⁻¹) 435 m, 474 s; ir in hexane in KBr cell (cm⁻¹) 682 s, 702 s, 740 s, 807 m, 900 w, 975 m, 1070 s, 1088 s, 1260 m, 1325 w, 1422 w, 1485 m, 1587 m, 3070 m.

Bis(1,4-difluorobenzene)vanadium(0) [(1,4-C₆H₄F₂)₂V]. The compound is red-amber (1% yield) and only slightly air sensitive in crystalline form and sublimes at 25° (<1μ) (large rectangular crystals can be produced this way): mass spectrum at 24 eV M (6), C₆H₄F₂V (5), C₆H₃FV (6), C₆H₄F₂ (57), C₆H₄F (6), V (3), V³⁺ (100); far ir and ir in hexane in KBr cell (cm⁻¹) 425 w, 440 m, 480 m, 485 sh, 495 sh, 510 m, 700 s, 730 s, 740 s, 835 s, 1165 m, 1185 m, 1205 vs, 1225 sh, 1482 w, 1525 s, 1695 w, 3080 w.

Bis(benzotrifluoride)vanadium(0) [(C₆H₅CF₃)₂V]. This material is orange (22% yield) and only slightly air sensitive in crystalline form, decomposes at 80–90°, and sublimes at 25° (<1μ): mass spectrum at 24 eV M (13), C₆H₅CF₃V (11), C₆H₅CF₃V (5), C₆H₄CF₃V (20), C₆H₅CF₃ (100), C₆H₅CF₂ (54), C₆H₅F (19), C₆H₅ (6), VF₂ (13), V (4), V³⁺ (5); far ir in hexane in polyethylene (cm⁻¹) 435 s, 482 m, 539 m, 552 m; ir in hexane in KBr cell (cm⁻¹) 658 m, 680 w, 695 m, 765 s, 808 s, 980 m, 1030 w, 1040 w, 1055 s, 1070 w, 1105 sh, 1127 vs, 1170 vs, 1265 s, 1310 vs, 1320 sh, 3080 w.

Bis(benzotrifluoride)chromium(0) [(C₆H₅CF₃)₂Cr]. The compound is yellow (26% yield) and slightly air sensitive, mp 90–91.5°, and decomposes at 170° in air or in sealed tube: mass spectrum at 24 eV M (22), C₆H₅CF₃Cr (44), C₆H₅CF₂Cr (6), C₆H₅CF₃ (18), C₆H₅CF₂ (100), C₆H₅CF (18), C₆H₅ (18), CrF (4), Cr (44); far ir and ir in KBr pellet (cm⁻¹) 440 s, 492 s, 500 s, 580 s, 655 s, 683 s, 765 w, 810 s, 880 s, 930 m, 990 m, 1005 m, 1050 s, 1110 s, 1140 s, 1175 s, 1265 s, 1315 s, 1405 s, 1450 m, 1490 s, 1585 w, 1660 w, 1700 w, 1770 w, 1800 w, 1820 w, 1850 w, 1870 w, 2780 w, 2985 w, 3080 m; nmr in cyclohexane shows broad singlet δ 4.91 (2 H), broad singlet δ 4.61 (3 H).

Bis(1,3-bis(trifluoromethyl)benzene)chromium(0) [(1,3-C₆H₄(CF₃)₂)₂Cr]. This compound is yellow-green (17% yield), air stable, mp 91.5–92.5°, decomposes at 200° in air or sealed tube, and sublimes slowly at 25° (10 μ) or rapidly at 100° (10 μ): mass spectrum at 70 eV M (7), C₆H₄(CF₃)₂Cr (22), C₆H₄C₂F₅Cr (20), C₆H₄(CF₃)₂ (17), C₆H₄C₂F₅ (100), C₆H₄C₂F₄ (81), C₇H₄F₄ (6), C₆H₄C₂F₃ (10), C₆H₄CF₃ (31), C₈H₃F₂ (4), C₆H₃Cr (22), CF₃ (9), Cr (96); far ir and ir in KBr pellet (cm⁻¹) 420 w, 440 m, 450 w, 500 s, 565 m, 580 m, 600 w, 675 s, 700 m, 750 w, 824 s, 840 s, 875 w, 888 m, 995 m, 1050 s, 1080 s, 1120 s, 1140 s, 1168 s, 1180 s, 1280 s, 1295 s, 1335 s, 1345 s, 1400 m, 1460 w, 1495 m, 1525 w, 1545 w, 1562 w, 3120

w; nmr in cyclohexane shows singlets at δ 3.62, 4.00; carbon and hydrogen analyses were satisfactory.

Bis(1,4-bis(trifluoromethyl)benzene)chromium(0) [(1,4-C₆H₄(CF₃)₂)₂Cr]. This material is amber colored (38% yield) and air stable; large parallelepiped plate crystals can be grown in hexane (mp 150–152°) and decompose at 266° in air or in a sealed tube and sublime at 40° (10 μ) or rapidly at 100° (10 μ): mass spectrum at 70 eV M (38), C₆H₄(CF₃)₂Cr (7), C₆H₄C₂F₅Cr (10), C₆H₄(CF₃)₂ (5), C₆H₄C₂F₅ (100), C₆H₄C₂F₄ (44), C₆H₄CF₃ (73), C₇H₄F₂ (33), C₆H₃ (14), CF₃ (26), Cr (38); far ir and ir in KBr pellet (cm⁻¹) 400 w, 458 s, 515 s, 580 m, 655 m, 680 m, 710 m, 750 m, 790 w, 840 s, 900 s, 1000 s, 1065 s, 1088 s, 1120 s, 1175 s, 1268 w, 1320 s, 1375 m, 1480 m, 1545 w, 1690 w, 1755 w, 1765 w, 1830 w, 1855 w, 3100 w; nmr in cyclohexane shows singlet at δ 3.65; the X-ray crystal structure study is in progress and confirms the structure given.

Bis(o-chlorobenzotrifluoride)chromium(0) [(o-C₆H₄CF₃)₂Cr]. This compound is yellow-green (33% yield), air stable, mp 81–82.5°, decomposes rapidly at 165° in air or in a sealed tube, and sublimes at 25° (10 μ) and rapidly at 100° (10 μ): mass spectrum at 70 eV M (2), M - Cl (1), C₆H₄C₁CF₃ (5), C₆H₄C₁CF₂ (100), C₆H₄CF₃ (8), C₆H₄CF₂ (43), C₆H₄Cl (10), C₆H₄CF (60), CrCl (4), C₆H₃ (41), CrF (7), CF₃ (5), Cr (15), CF₂ (19); far ir and ir in KBr pellet (cm⁻¹) 405 m, 468 s, 500 s, 510 s, 590 s, 640 s, 670 m, 700 s, 780 s, 820 s, 880 m, 865 m, 915 m, 925 m, 1012 s, 1030 s, 1075 s, 1125 s, 1170 s, 1230 s, 1307 s, 1390 s, 1405 s, 1422 m, 1480 m, 1505 w, 1522 m, 1610 w, 1650 w, 1680 w, 1700 w, 1745 w, 1790 w, 1820 w, 1840 w, 1865 w, 3070 w, 3110 w; nmr in cyclohexane shows singlets at δ 3.55 and 3.62; carbon and hydrogen analyses were satisfactory.

Registry No. [(C₆H₅F)₂V], 53966-09-9; [(C₆H₅Cl)₂V], 53966-10-2; [(1,4-C₆H₄F₂)₂V], 53966-04-4; [(C₆H₅CF₃)₂V], 53966-11-3; [(C₆H₅CF₃)₂Cr], 53966-07-7; [(1,3-C₆H₄(CF₃)₂)₂Cr], 53966-05-5; [(1,4-C₆H₄(CF₃)₂)₂Cr], 53966-06-6; [(o-C₆H₄CF₃)₂Cr], 53966-08-8.

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