and cyclopropylcarboxaldehydes[9] allows for the synthesis of chiral 2-methyl 1,3-diols using the oxymercuration of the corresponding cyclopropylcarbinols. For the synthesis of the more highly oxygenated natural products the carbon mercury bond of the intermediate organomercurial can be converted into a carbon oxygen bond.[10]

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## Metal Vapor Synthesis of a Novel Triple-Decker Sandwich Complex: (η6-Mesitylene)2(μ-η6:η6-mesitylene)Cr2

William M. Lamanna

3M Central Research Laboratories
St. Paul, Minnesota 55144

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The reaction of transition-metal vapors with arene substrates is a well-established route to a host of bis(arene)metal sandwich complexes, some of which are difficult or impossible to prepare by more conventional methods.[1,2] We wish to report here preliminary evidence which indicates that under conditions of high metal loadings these reactions can lead to the formation of oligomeric byproducts formulated as *multiple-decker sandwich complexes*.

Cocondensation of chromium vapor with neat mesitylene in a rotary metal atom reactor[3] produces the expected complex (η6-mesitylene)2Cr (**1**). When the reaction is conducted at high metal to ligand ratios a previously undetected byproduct formulated as the novel triple-decker sandwich complex (η6-mesitylene)2(μ-η6:η6-mesitylene)Cr2 (**2**) is formed.[4] In pure form, the
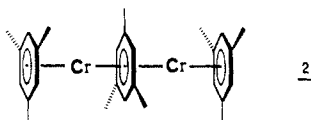
bimetallic triple-decker exists as a dark, crystalline solid.[5] Despite its high molecular weight, the complex is readily soluble in ethers and aliphatic and aromatic hydrocarbons. Solutions of **2** are deep red and extremely oxygen sensitive; air exposure leads to rapid conversion to **1**, free mesitylene, and chromium oxide. The complex exhibits reasonably good thermal stability, decomposing slowly above 70 °C to a mixture of **1**, free mesitylene, and chromium metal.

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(4) Cocondensation was conducted at 10^{-6} torr with cooling provided by a liquid nitrogen bath. Chromium was sublimed by resistive heating in dual, alumina-coated, tungsten wire crucibles at a rate of 0.75 g/h. Mesitylene was introduced through a heated shower head assembly at a rate of 1.25 mL/min. Reaction of 1.41 g of chromium with 130 mL of mesitylene under these conditions produced a dark frozen matrix which was allowed to thaw in vacuo. The resulting deep red solution was filtered through Celite and the filtrate evaporated to dryness at 10^{-3} torr and 40 °C. The remaining organometallic residue contained a 7.3/1.0 ratio of **1** and **2**, respectively, according to ^{1}H NMR analysis. The bis(mesitylene)chromium was sublimed at 65–70 °C and 10^{-3} torr leaving a nonvolatile residue which was enriched in **2**. This residue was recrystallized twice from petroleum ether at −30 °C yielding 100 mg of pure **2** in the form of dark thin plates.

(5) Attempts to grow single crystals suitable for X-ray crystallography have thus far been unsuccessful.

Although there exist numerous examples of multiple-decker sandwich complexes containing from two to five metal atoms in a single chain,[6-15] complex **2** is the first homoleptic complex of this type containing all arene ligands. Only one other compound in this class, (η5-C5H5)2(μ-η6:η6-arene)V2, possesses an η6-arene ring symmetrically bridging two metal centers.[11] The (mesitylene)3Cr2 triple decker is formally a 30-electron complex and thus obeys the 30/34 electron rule put forth by Hoffmann et al. to account for the stability of certain triple-decker sandwiches.[16] A more recent theoretical analysis predicts the stability of structure **2** on the basis of HOMO–LUMO energy gap arguments.[17]

The proposed stoichiometry in **2** was established by elemental analysis (±0.6% for C, H, and Cr). Formulation of the triple-decker sandwich structure is based on evidence for ^{1}H and ^{13}C NMR spectroscopy. The chemical shift and coupling constant data for **2** are summarized below:[18] ^{1}H δ 3.4 (s, 6 H, Ar ^{1}H of terminal arenes), 2.9 (s, 3 H, Ar ^{1}H of bridging arene), 2.5 (s, 9 H, Me ^{1}H of bridging arene), 2.1 (s, 18 H, Me ^{1}H of terminal arenes); ^{13}C δ 82.5 (s, $C_{1,3,5}$ of terminal arenes), 74.9 (d, $^1J_{C-H}$ = 164 Hz, $C_{2,4,6}$ of terminal arenes), 64.7 (s, $C_{1,3,5}$ of bridging arene), 60.6 (d, $^1J_{C-H}$ = 171 Hz, $C_{2,4,6}$ of bridging arene), 21.2 (q, $^1J_{C-H}$ = 125 Hz, Me's of bridging arene), 20.3 (q, $^1J_{C-H}$ = 125 Hz, Me's of terminal arenes).

Both the ^{1}H and ^{13}C NMR spectra reveal the presence of mesitylene ligands in two different coordination environments and in the ratio of 2:1. The narrow line widths (<2 Hz) indicate that the complex is diamagnetic as would be expected for a 30-electron triple-decker sandwich structure.[16] The magnetic equivalency of related hydrogens and carbons in each arene ring is consistent with the high degree of symmetry in **2**. No evidence of fluxional behavior is apparent in the ^{1}H or ^{13}C NMR spectra down to −90 °C.[19] A noteworthy feature is the significant upfield shift of the

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(18) ^{1}H NMR spectra were recorded at 90 and 200 MHz; ^{13}C spectra were recorded at 50 MHz. NMR samples were prepared in toluene-d_8 or benzene-d_6. Chemical shifts are referenced to solvent resonances.

(19) The NMR data does not strictly rule out the existence of a less symmetrical butterfly structure similar to that found in the binuclear vanadium complex (C5H5)2(C6H6)V2H2;[20] however, such a formulation would require that fluxional rotation of the face-bridging arene ring proceed with a very low activation barrier (<8 kcal/mol) and does not easily account for the matrix isolation evidence for the formation of higher nuclearity oligomers (vide infra).

ring ^{1}H and ^{13}C signals of the bridging arene relative to the corresponding resonances of the terminal arenes in **2** or bis-(mesitylene)chromium.[21] These shifts may arise from the electronic effects of two chromium atoms coordinated to a single bridging mesitylene[21] or anisotropic shielding by the two terminal arene rings.

In order to probe the mechanism of triple-decker sandwich formation, a matrix isolation study of the reaction of chromium vapor with mesitylene was undertaken. Microscale reactions were conducted in a Torromis matrix isolation unit[22a] by evaporation of chromium into a 5% methylcyclohexane solution of mesitylene cooled to 140 K on a sodium chloride window. The progress of the reaction was followed by monitoring changes in the UV–vis spectrum as a function of metal loading. At low Cr concentrations a single band centered at 331 nm is observed. This peak is identical with the high-energy absorption arising from a genuine sample of **1** and is thus assigned to the charge-transfer band of the bis-(arene) complex.[23] At higher Cr loadings the 331-nm band increases in intensity and two new red-shifted bands centered at ca. 438 and 518 nm begin to appear. The 438-nm transition is attributed to the formation of the triple-decker sandwich complex. An authentic sample of **2** exhibits a single intense band at this wavelength. The appearance of **2** at the latter stages of the metal atom reaction suggests that the triple-decker sandwich complex is formed by competitive trapping of Cr atoms by mesitylene and **1**. The identity of the complex that gives rise to the 518-nm absorption is still in question. It is tempting to speculate that this band results from formation of the tetradecker sandwich, (mesitylene)$_4$Cr$_3$, via trapping of Cr^0 by 2 equiv of **1** or 1 equiv each of mesitylene and **2**. Attempts to isolate the tetradecker from preparative-scale reactions have thus far been unsuccessful.

It is interesting to note that Ozin and co-workers have conducted similar matrix isolation studies of the reactions of Cr, Mo, Ti, and V vapor with a number of monomeric and polymer-supported arene substrates and with bis(arene)metal complexes. Qualitatively, the changes observed in the UV–vis spectra as a function of metal loading are identical with those reported herein. In numerous accounts of this work,[22] the appearance of a series of bands, red-shifted from the original bis(arene)metal absorption, is interpreted as evidence for the formation of "arene-stabilized metal clusters" of general structure **3**. The authors propose that the clusters are produced by stepwise addition of metal atoms to the central metal of the initially formed bis(arene)metal complex **3** ($n = 1$). Nuclearities as high as $n = 5$ have been reported.

The structure and stoichiometry represented by **3** are clearly inconsistent with our analytical and NMR data for the bimetallic mesitylene complex **2**. Based on this work, a reformulation of the purported "arene-stabilized metal clusters" as multiple-decker sandwich oligomers of general structure **4** would appear to be in
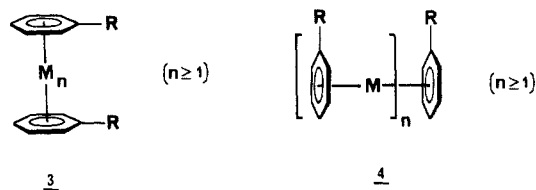
order, at least in the case of chromium. The likelihood that Ti, V, and Mo react in a similar fashion must be strongly considered

and is currently under investigation in our lab.

Theoretical support for the existence of *extended* multiple-decker sandwich complexes comprised of long chains of alternating arene and metal units was recently established by the calculations of Burdett and Canadell[17] which indicate that the benzene–chromium multiple-decker sandwich polymer should be thermally stable. The band structure associated with such polymers and the proximity of adjacent metal centers are expected to lead to anisotropic electrical, magnetic, and optical properties. Of particular interest is the potential for one-dimensional conductivity in the mixed-valence form. The chemical and physical properties of **2** should serve as a valuable model for the more extended polymeric systems and may provide clues to the efficient synthesis of higher oligomers.

Supplementary Material Available: Analytical data, NMR, and UV–vis spectra for **2** and series of absorption spectra from matrix isolation study (5 pages). Ordering information is given on any current masthead page.

Excited Triplet State Resonance Raman Spectra of Magnesium, Zinc, and Palladium Tetraphenylporphine

Dongho Kim,[†] James Terner,[‡] and Thomas G. Spiro*[†]

Department of Chemistry, Princeton University
Princeton, New Jersey 08544
Department of Chemistry, Virginia Commonwealth
University, Richmond, Virginia 23284

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There is wide interest in the electronic states of metallo-porphyrins because of their rich and varied spectroscopy, their utility as electron-transfer and photoactive agents, and the multifaceted roles of heme and chlorophyll groups in biology.[1] Resonance Raman (RR) spectroscopy has produced much useful information about the structures of metalloporphyrins in their ground states[2] and can be expected to help elucidate excited states. Down shifts and broadening in the picosecond RR spectrum of the oxyhemoglobin photoproduct[3] have been interpreted as arising from unrelaxed electronic excitation of the deoxy-heme. We now report RR spectra of the lowest triplet excited states of magnesium, zinc, and palladium tetraphenylporphine (TPP).

Figure 1 shows RR spectra of ZnTPP in dichloromethane, obtained with 476.5 Ar$^+$ CW laser excitation. ZnTPP fluoresces strongly, but the emission is from the low-energy Q-band (λ_{max} = 589 nm)[4] and does not interfere with RR spectra obtained with blue excitation. The bottom spectrum was obtained with the sample in an ordinary spinning cell and is the RR spectrum of ground-state ZnTPP;[5] frequencies and assignments[6] are listed in

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* Author to whom correspondence should be addressed.

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