

perature for 7 h. After evaporation of the solution to dryness in vacuo, the residue was chromatographed on neutral alumina with hexanes/CH₂Cl₂ (2:1) as the eluent. The yellow band was collected and reduced in volume under vacuum. Cooling the concentrated solution to -70 °C gave air-stable, pale yellow crystals (70% yield) of **2**.¹⁶ As in **1**, the ¹H and ¹³C NMR spectra of **2** show two upfield protons (δ 4.16 d, H₂; 3.18 d of d, H₃; 7.01 d of d, H₄; 6.29 d, H₅) and two upfield carbons (δ 44.0, 51.1, 119.1, 140.9), which indicate the presence of the η^2 -selenophene.

The PPh₃ derivative of **2** was prepared in the same manner from Cp*(CO)₂Re(η^2 -Sel) (60 mg, 0.12 mmol) and W(CO)₄(PPh₃)(THF), generated by UV photolysis of W(CO)₅(PPh₃) (90 mg, 0.15 mmol) in THF. Crystals of air-stable, pale yellow **3**¹⁷ (73% yield) were obtained from hexanes/CH₂Cl₂ (2:1) at -70 °C. An X-ray diffraction study¹⁸ of **3** shows (Figure 1) the selenophene ring to be planar. The Re-coordinated C(2)-C(3) distance (1.44 (2) Å) is substantially longer than that (1.369 (1) Å) in free Sel,¹⁹ while the uncoordinated C(3)-C(4) and C(4)-C(5) distances (1.44 (2) and 1.34 (2) Å, respectively) are nearly the same as those (1.433 (3) and 1.369 (1) Å, respectively) in free Sel. Although the C(2)-Se-C(5) angle (86.3 (5)°) is essentially the same as that (87.46 (4)°) in free Sel,¹⁹ the C(2)-Se and C(5)-Se distances (1.95 (1) and 1.92 (1) Å) are considerably longer than in Sel (1.855 (1) Å).¹⁹ As in S-coordinated thiophene complexes, the Se in **3** is pyramidal, as indicated by the angle (112.1 (6)°) between the W-Se vector and the vector from Se to the midpoint of the line from C(2) to C(5). The corresponding angle in Cp*(CO)₂Re(T) is 140°. ²⁰ From the above data, it is clear that the structure of the selenophene has been changed significantly as a result of its coordination to the two metals. The lengthening of the C-Se bonds is especially interesting because it is the analogous C-S bonds in thiophenes that must be cleaved on HDS catalysts.

A question that arises in this work is why selenophene is η^2 -bonded to Cp*(CO)₂Re and thiophene is S-bonded. A possible explanation is that the π -system of selenophene, which has been suggested to be more electron rich than that of thiophene,²¹ would form a stronger π -donor bond to the Re than would thiophene. On the other hand, the relative π -accepting properties of Sel and T, as well as the coordinating abilities of the Se and S atoms, are also involved; thus it is not clear at this time what factors determine the coordination modes of these ligands.

Acknowledgment. We are grateful to Dr. Lee M. Daniels of the Iowa State University Molecular Structure Lab for determining the structure of **3**.

(16) **2**: IR (hexanes) ν (CO) 2076 (w), 1980 (m), 1940 (s), 1932 (s), 1924 (s), 1912 (m) cm⁻¹; ¹H NMR (CDCl₃) δ 7.01 (d of d, 1 H, Sel), 6.29 (d, 1 H, Sel), 4.16 (d, 1 H, Sel), 3.18 (d of d, 1 H, Sel), 2.01 (s, 15 H, Cp*); ¹³C NMR (CDCl₃) δ 204.9, 200.9, 198.1 (CO), 140.9, 119.1, 51.1, and 44.0 (Sel), 99.0 (C of Cp*), 10.1 (Me of Cp*); EIMS (70 eV) *m/e* 778 (M⁺ - 2CO, based on ¹⁸⁷Re and ⁸⁰Se), 750 (M⁺ - 3CO), 722 (M⁺ - 4CO), 694 (M⁺ - 5CO), 510 (M⁺ - W(CO)₅). Anal. Calcd for C₂₁H₁₉O₇ReSeW: C, 30.30; H, 2.30. Found: C, 30.58; H, 2.34.

(17) **3**: IR (hexanes) ν (CO) 2014 (m), 1955 (m), 1908 (m), 1873 (s), 1852 (s) cm⁻¹; ¹H NMR (CDCl₃) δ 7.53-7.38 (m, 15 H, PPh₃), 6.82 (d of d, 1 H, Sel), 5.29 (d, 1 H, Sel), 4.32 (d, 1 H, Sel), 3.19 (d of d, 1 H, Sel), 1.97 (s, 15 H, Cp*).

(18) Crystallographic data for **3**: Pale yellow crystals of **3**·1.5CH₂Cl₂ were grown from CH₂Cl₂/hexanes at -70 °C; triclinic, space group P $\bar{1}$ (No. 2); *a* = 13.390 (5) Å, *b* = 13.812 (6) Å, *c* = 12.559 (3) Å; α = 116.89 (2)°, β = 95.89 (2)°, γ = 86.66 (2)°; *V* = 2060 (1) Å³; *d*_{calcd} = 1.915 g/cm³; *Z* = 2; μ = 69.77 cm⁻¹ (Mo K α). Diffraction data were collected at -75 ± 1 °C by using an Enraf-Nonius CAD4 automated diffractometer. A total of 6723 reflections were collected. Of the 4980 unique data, 4085 reflections having *I* > 3 σ (*I*) were used to solve the structure. The positions of the Re, W, Se, and P atoms were given by direct methods. The remainder of the non-hydrogen atoms were located in difference Fourier maps following least-squares refinement of the known atoms. *R* = 4.8% and *R*_w = 6.4% (*w* = 1/ σ^2 (*I*_o)). Details of data collection and refinement are given in the supplementary material.

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Supplementary Material Available: Description of the data collection and structure solution, ORTEP drawing of **3**, tables of crystal data, positional and thermal parameters, complete bond distances and angles, and least-squares planes (15 pages); listing of calculated and observed structure factors for **3** (23 pages). Ordering information is given on any current masthead page.

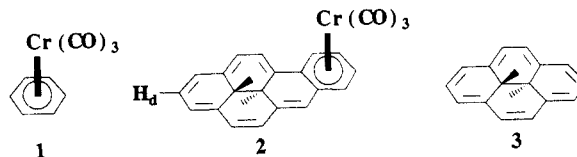
Synthesis of the First Metal-Complexed Benzannulene. An Estimate of the Aromaticity of Tricarbonylchromium-Complexed Benzene Relative to the Aromaticity of Benzene Itself

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The upfield shift of about 2 ppm of the protons in tricarbonylchromium-complexed benzene (**1**) has prompted much investigation of its origin.¹ Such shifts have been interpreted as a combination of effects including quenching of the ring current, withdrawal of electron density from the ring by the Cr(CO)₃ moiety, the magnetic anisotropy of the chromium-ligand bond, and partial rehybridization of the ring carbon atoms. The synthesis of **2**, the first annuleno-fused tricarbonylchromium-complexed benzene, permits a definitive statement to be made on the bond delocalization present in **1**, as well as an estimate of its effective resonance energy, relative to that of benzene.



The bridged 14 π annulene **3** (DMDHP, dimethyldihydropyrene) is an excellent probe for delocalization in fused aromatic systems such as **2** because the chemical shifts of the methyl protons are sensitive to the delocalization in the macrocyclic ring, yet are almost *invariant* to external substituents, even those with substantial anisotropic effects, because of the long distance involved (>5 Å) and the fact that the protons are three bonds separated from the π -periphery.^{2,3} These protons do however respond linearly to the amount of bond fixation in the macrocyclic ring, with δ ranging from +1 (100% bond fixation) to -4.2 (0% bond fixation) ppm. Fusion of an aromatic annelating ring to **3**, as in **2**, causes bond fixation of the macrocyclic ring, the degree depending on the relative aromaticities of **3** and the annelating ring (in this case **1**). The aromaticity (as measured by bond-fixing ability) of **1** relative to that of benzene can thus be estimated by comparison of the methyl proton chemical shifts of **2** with those of its uncomplexed derivative **4**.⁴ The synthesis of **2** (or an isomer) was thus undertaken.

No metal complexes of benzannulenes have been reported, perhaps in part because of the limited stability of most benzannulenes. Indeed heating **4** with Cr(CO)₆ or Cr(CO)₃(CH₃CN)₃ gave no complexed annulene, only decomposition. Since the

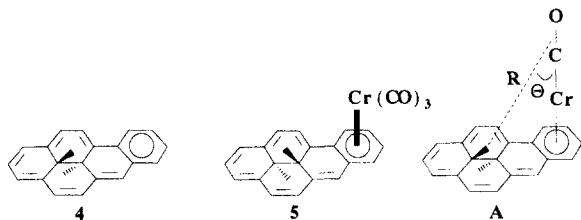
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benzene ring in **4** is more aromatic than that in naphthalene, exchange of ligand between **4** and (tricarbonylchromium)-naphthalene should and did occur in ether (containing catalytic THF) to give 60% of **2** as a mixture of two isomers in a 3:1 ratio. The major isomer was separated by chromatography and fractional crystallization, mp 189–190 °C, and was shown to be **2** by a preliminary X-ray determination.⁵ By NMR, the minor isomer is assigned the structure **5**. The chemical shifts found for the



internal methyl protons are as follows: **2**, δ -0.87 and -0.98; **5**, δ -0.81 and -1.16. For **2**, the methyl syn to the Cr is assigned⁶ the shift -0.87, and the methyl anti to the Cr is assigned the shift -0.98. The important point is that, despite the difference in positions of the two methyl groups relative to the center of anisotropy, the chemical shift difference between these methyl protons is very small. For a Cr(CO)₃ group, McGlinchey⁷ takes the center of anisotropy of a Cr(CO)₃ moiety to be 3.3 Å above the Cr along the C₃ axis (see A; the three carbonyl groups have been replaced by a "supercarbonyl" along the C₃ axis), and for **2** the relevant values of R and θ for the two methyl groups are 8.49 Å, 17.18° and 5.95 Å, 54.41° for the distal and proximal methyl groups, respectively. Based on McGlinchey's results,⁷ the calculated effects of the Cr(CO)₃ on these protons at these distances are only +0.00 and +0.16 ppm, respectively, in excellent agreement with the found difference in chemical shift for **2** of 0.11 ppm! Moreover, we have found previously that the chemical shift of the methyl protons correlates very well with the chemical shift of the distant ring proton H_d for a series of annelated annulenes;³ in **2**, H_d has $R = 8.68$ Å and $\theta = 63.88^\circ$ and thus is hardly affected by the Cr(CO)₃ at all. On the basis of its chemical shift of δ 6.88, we can calculate⁸ the expected chemical shift of the methyl protons to be δ -0.97. Since the found values agree very closely to this and are in accord with the McGlinchey equation results, we can conclude that, in **2**, the Cr(CO)₃ has almost no anisotropic effect on the chemical shift of the methyl protons. Why then is the chemical shift of the methyls (-0.97 ppm) at lower field than those of the uncomplexed annulene **4** (-1.62 ppm)? This could be because of more bond fixation in the macrocyclic ring of **2** than of **4**, or because of removal of electron density from the macrocyclic ring in **2** by the Cr(CO)₃. Substantial reduction of electron density in the macrocyclic ring in **2** is not supported by π -SCF calculations¹⁰ and is ruled out by examination of the coupling constants of **2** relative to those of **4**. If substantial removal of charge from the macrocyclic ring occurred,³ J values in **2** would be smaller than in **4**. However, those found¹¹ alternate more in **2** than in **4**, consistent with more bond fixation in the macrocyclic ring of **2** than **4**, in agreement with the chemical shift results. The inescapable conclusion, supported by the chemical shifts of the

(5) Satisfactory ¹H and ¹³C NMR and mass spectra and elemental analysis were obtained.

(6) Based on results of McGlinchey,⁷ where protons proximal to Cr are found most deshielded.

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(8) From Haddon's⁹ ring current geometry factors, the predicted sensitivity factor for the internal methyl protons relative to the external protons is 2.38. Comparison of the chemical shifts in a series⁴ of annelated dihydroxyrenes yields us the equation $\Delta\delta_{Me} = -2.60\Delta\delta_H - 0.029$ ($\rho = 0.9998$).

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(11) For **4**, $J_{1,2} = 8.87$ Hz, $J_{2,3} = 6.52$ Hz, $J_{4,5} = 8.83$ Hz, and $J_{11,12} = 6.57$ Hz. For **2**, $J_{1,2} = 8.97$ Hz, $J_{2,3} = 6.30$ Hz, $J_{4,5} = 9.24$ Hz, and $J_{11,12} = 6.53$ Hz.

methyl and distant protons, the increased alternation in coupling constants, and π -SCF calculations, is that a tricarbonylchromium-complexed benzene ring has more bond-fixing power, and resists bond fixation in itself more than benzene does, and is thus more "aromatic" than benzene! Using our recently developed³ equation to estimate resonance energies of the annelating ring in annelated dimethyldihydroxyrenes, we estimate that, on the basis of its bond-fixing ability, **1** thus has about 1.3 times the "resonance energy" of benzene. We are attempting to prepare other metal-complexed derivatives of **3** and **4** and thus compare them with **2**.

Can CO₂ Coordinate to a Ni(I) Complex? An ab Initio MO/SD-CI Study

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CO₂ conversion into useful substances has been an attractive object of research.¹ One of the effective attempts is electrocatalytic reduction of CO₂.^{2–15} In those investigations, transition-metal CO₂ complexes have often been postulated as a key intermediate.^{3a,7b,8,13–15} In this work, Ni^I(NH₃)₄(CO₂) (**1**), [Ni^I(NH₃)₄(CO₂)]⁺ (**2**), and [Ni^{II}F(NH₃)₄(CO₂)]⁺ (**3**) are investigated with the ab initio MO/SD-CI method. These complexes can be viewed as models of an intermediate in electrocatalytic reduction of CO₂ with Ni(cyclam)Cl₂,⁷ where (NH₃)₄ and F are models of cyclam and Cl, respectively (note that an intermediate Ni–CO₂ complex was proposed to be a Ni^I species⁷). One important conclusion is that CO₂ can coordinate with Ni^IF(NH₃)₄ to form a stable η^1 -CO₂ complex but not with [Ni^I(NH₃)₄]⁺ and [Ni^{II}F(NH₃)₄]⁺.

Spin-restricted ab initio MO/SD-CI calculations were carried out with the MELD program,¹⁶ in which split-valence type basis sets¹⁷ were used with the exception of minimal basis sets for Ni^{18a} and H^{18b} and a triple- ζ basis set for the Ni 3d orbital.¹⁹ The

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