

notonous relationship when all π -acid ligands are considered. By way of example, the cases of CO and pyridine can be compared. The affinity of the former ligand is certainly greater than that of the latter.^{6,7} The pyridine complex of pentaaminerruthenium(II) has a very strong absorption with a maximum at 407 nm,⁸ while no absorptions of the CO duplex are observed at wavelengths above 210 nm which are not ascribable to d-d transitions (weak absorption in the 270–280 range).⁹

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1,9-Dimethyldibenzo[*b,f*]pentalene Dication and Dianion. New 14π and 18π Aromatic Systems

Sir:

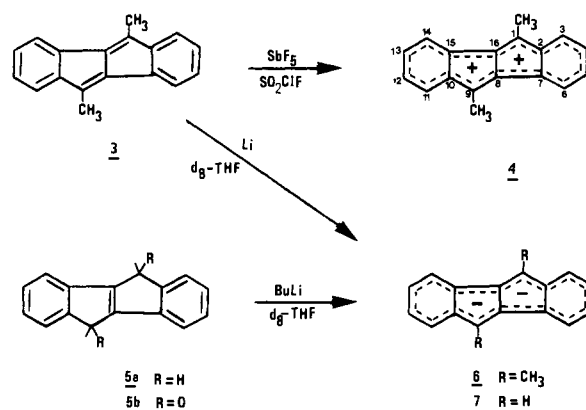
Fused conjugated systems containing $4n\pi$ electrons, similar to the monocyclic cyclooctatetraene¹ and [12]annulene,² may in principle acquire aromaticity by oxidation to the corresponding dication, or by formation of the dianion. These ions are predicted to behave like peripheral aromatic systems containing $(4n + 2)\pi$ electrons.³ The pentalene dianion,⁴ heptalene dianion,⁵ and dibenzononalene dianion⁶ were prepared and exhibited aromatic character. The preparation of **2**, the $8C-6\pi$ aromatic dication of the unknown pentalene (**1**) has proved to be unusually difficult: several attempts to



prepare derivatives of **2** by chemical or electrochemical methods proved to be unsuccessful.⁷ The difficulties in preparing derivatives of **2** were interpreted in terms of steric hindrance to delocalization in protonated dibenzo[*cd,gh*]-

pentalenequinone^{7a} and partial antiaromatic character of the cyclopentadiene cation moieties.^{7c} We wish to report the preparation and characterization of the benzannulated pentalene dication and dianion and to show that the system may acquire aromaticity by conversion either to the dication or dianion.

Upon treatment of 1,9-dimethyldibenzo[*b,f*]pentalene (**3**)⁸ with SbF_5 in SO_2ClF at $-78^\circ C$, the two-electron oxidation product 1,9-dimethyldibenzo[*b,f*]pentalene dication (**4**) was obtained. The 1H NMR spectrum (Table I) of the dark green solution consists of two triplets at 9.72 and 9.40 ppm attributed to $H_4, H_5, H_{12},$ and H_{13} and two doublets at 9.84 and 9.49 ppm attributed to $H_3, H_6, H_{11},$ and H_{14} . No spectral change was noted over the temperature range -40 to $0^\circ C$.



The observed average proton downfield shift accompanying the transformation $3 \rightarrow 4$ is 2.8 ppm. It was shown in a series of charged aromatic molecules that the 1H chemical shifts are a linear function of the electron density.⁹ On this basis, the average proton downfield shift $\Delta\delta$ accompanying the oxidation process $3 \rightarrow 4$ is expected to be 1.4 ppm. The observed chemical shifts difference is significantly enhanced (by 1.4 ppm) and is attributable to the formation of a diamagnetic ring current. Noteworthy is the deshielding observed in the chemical shift of the aromatic protons indicating the delocalization of all 14π electrons in **4**. The chemical shifts of the methyl substituents (4.08 ppm) correlate nicely to other methyl derivatives of dicationic species.^{1a,10}

Further support to the dicationic nature of **4** is obtained by comparison of the ^{13}C NMR of **3** and **4**. Oxidation of **3** resulted in a significant downfield shift. The observed average ^{13}C chemical shift $\Delta\delta_c$ in the transformation $3 \rightarrow 4$ is ~ 368 ppm or 184 ppm/e. This value is very near to that observed for other polycyclic dications^{1b,11} which is very similar indeed to the magnitude predicted by the Spiescke-Schneider relationship.^{9a,12} The resonances of the fused benzene carbon atoms appear at a considerably lower field than those in **3**; hence delocalization of all 14π electrons, as deduced by 1H NMR is occurring.

Treatment of **3** with lithium wire or deprotonation of 1,9-dihydrodibenzo[*b,f*]pentalene (**5a**)¹³ with BuLi in THF- d_8 yielded dianions **6** and **7**, respectively.¹⁴ The 1H NMR spectra

Table I. 1H NMR Parameters for Dibenzof[*b,f*]pentalene Dication, Dianions, and Related Compounds^a

	H_3, H_6, H_{11}, H_{14}	H_4, H_5, H_{12}, H_{13}	R
3 ^b		7.12 (m), 6.89 (m)	2.17 (s) ^c
4 ^d	9.84 (d, $J = 9$ Hz), 9.49 (d, $J = 8$ Hz)	9.72 (t, $J = 7.6$ Hz), 9.40 (t, $J = 7$ Hz)	4.08 (s) ^c
5 ^b		7.25 (m)	3.53 (s) ^e
6 ^f	7.57 (d, $J = 7$ Hz), 7.27 (d, $J = 8$ Hz)	7.17 (t, $J = 7$ Hz), 6.91 (t, $J = 8$ Hz)	3.10 (s) ^c
7 ^f	7.65 (d, $J = 8$ Hz), 7.24 (d, $J = 8$ Hz)	6.80 (dd, $J_1 = 8$ Hz, $J_2 = 6$ Hz), 6.54 (dd, $J_1 = 8$ Hz, $J_2 = 7$ Hz)	5.90 (s) ^e

^a Chemical shifts are in δ (parts per million) from Me_4Si in a capillary. ^b In $CDCl_3$ solution at $32^\circ C$. ^c Bruker WH-270 of the Weizmann Institute of Science, Rehovot, Israel. ^d In $SO_2ClF-SbF_5$ solution using acetone- d_6/Me_4Si capillary at $-78^\circ C$. ^e Varian HA 100 D. ^f In THF- d_8 solution.

of **6** and **7** are very similar (Table I). The chemical shifts of **6** and **7** are a result of two transverse factors: an upfield shift due to shielding of the negative charges and a downfield shift due to the formation of a diamagnetic ring current in the expected aromatic dianion. The expected average upfield shift due to π -electron shielding is 1.4 ppm.⁹ However, the transformation of neutral hydrocarbons into the dianionic species **6** and **7** does not displace the center of gravity of the chemical shifts despite the negative charges. Noteworthy are the signals of the fused benzene protons which appear at lower field relative to the neutral hydrocarbon **3**. These results clearly indicate the formation of a diamagnetic ring current in the aromatic dianions **6** and **7**, and they may be considered as perturbed peripheral [16]annulene dianions. Quenching of **7** with D₂O yielded **5b**: deuteration at positions 1 and 9, the most deshielded positions as emphasized by the ¹H NMR.

From all of the above, it may be concluded that 1,9-dimethylidibenzo[*b,f*]pentalene (**3**) can either be oxidized or reduced to the respective dicationic and dianionic species. The dication **4** and dianions **6** and **7** are delocalized diatropic aromatic systems. From the ¹H NMR shifts of the benzene rings fused to the pentalene moiety, we deduce that these charged species behave like peripheral [16]annulene dication and dianion, respectively. To our knowledge, this is the first example of a fused 4n π polycyclic system including a pentalene nucleus, to show aromatic character as both dication and dianion. We are extending our investigations by examining the possibility of generating the charged species, prepared chemically in the present work, by electrochemical methods.

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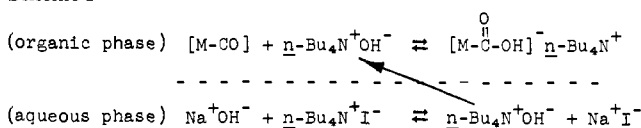
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Phase-Transfer Catalyzed Oxygen-18 Labeling Studies of Carbonyl Ligands in Neutral Metal Carbonyl Derivatives

Sir:

Recently we have reported on the incorporation of oxygen-18 into cationic metal carbonyl derivatives of manganese and rhenium.¹⁻⁴ This process was proposed to proceed via neutral

Scheme I



metal carbonyl intermediates containing the hydroxycarbonyl ligand, i.e., $L_n(\text{CO})_{5-n}\text{M}(\text{COOH})$ ($n = 0-2$) species. Furthermore, it was shown that in substituted metal carbonyl derivatives, where there are two electronically different CO groups, the oxygen atoms on the more electron-poor carbonyl ligands (i.e., carbonyl groups with the larger CO stretching force constant⁵) were exchanged at a faster rate. Thus, it was possible to afford stereospecifically labeled metal carbonyl derivatives employing the H₂¹⁸O exchange reaction. In addition the corollary observation that the relative rates of oxygen exchange decrease with increasing substitution at the metal center with electron donating ligands was noted, $\text{M}(\text{CO})_6^+ > \text{M}(\text{CO})_5\text{L}^+ \gg \text{M}(\text{CO})_4\text{L}_2^+$. The $L_n(\text{CO})_{5-n}\text{M}(\text{COOH})$ intermediates were also found to undergo CO₂ elimination with metal hydride formation, a process common to the energy-important metal-catalyzed water-gas shift reaction.⁶⁻⁸

To understand these processes more fully we have begun studies to investigate the conditions for oxygen exchange in neutral metal carbonyl derivatives. In this communication we wish to report on phase-transfer catalyzed oxygen-18 labeling studies of the carbon monoxide ligands bound to neutral group 6b and iron metals.

Although the cationic hexacarbonyl derivatives of the group 7b metals readily undergo oxygen-exchange reactions with H₂¹⁸O, the neutral isoelectronic group 6b analogues were found to be totally inert under similar reaction conditions.^{2,9} On the other hand, we have shown that the rate of oxygen exchange between metal bound CO and H₂O is greatly accelerated in the electron-rich $[\text{Mn}(\text{CO})_4(\text{diphos})]^+$ derivative if trace quantities of triethylamine are added to the reaction solution.³ Therefore, it should be possible to enhance the rate of reaction of the less electrophilic carbonyl groups in the group 6b metal derivatives by raising the pH of the solution. This was accomplished using a biphasic reaction system with the organic phase consisting of the neutral carbonyl derivative in benzene and an aqueous phase consisting of sodium hydroxide with a small quantity of tetra-*n*-butylammonium iodide as the phase-transfer catalyst (Scheme I). The complexes we have initially examined include $\text{M}(\text{CO})_5\text{L}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$, and $\text{L} = \text{CO}, \text{PPh}_3$, and $\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5$; and $\text{M} = \text{Cr}$ and $\text{L} = n\text{-Bu}_3\text{P}$) and $\text{Fe}(\text{CO})_4\text{PPh}_3$ derivatives.

In a typical experiment, a 0.05-mL sample of 11.3 M Na¹⁸OH solution (prepared by equilibrating 0.090 g (2.24 mmol) of NaOH in 0.20 mL of 99% enriched H₂¹⁸O) was added to a mixture of 0.0420 g (0.119 mmol) of $\text{W}(\text{CO})_6$ and 0.010 g (0.027 mmol) of *n*-Bu₄NI dissolved in 5.0 mL of dry benzene under a nitrogen atmosphere. The resulting two-phase system was heated at 75 °C with vigorous stirring. Samples (0.50 mL) were withdrawn at various time intervals and the solvent mixture removed in vacuo. The samples were redissolved in 0.60 mL of hexane and their ν_{CO} infrared spectra were recorded in 1.0-mm NaCl sealed solution cells.

Figure 1 illustrates representative ν_{CO} spectral traces obtained during the course of oxygen-18 incorporation into a group 6b metal carbonyl derivative, $\text{W}(\text{CO})_6$. It was possible to assign all the observed bands in all the complexes studied to the various C¹⁸O substituted species by noting the rates of appearance and decay of bands concomitantly aided by calculations involving a restricted CO force field.¹⁰

We have been able to discern from a detailed analysis of these ν_{CO} spectral results in the $\text{M}(\text{CO})_5\text{L}$ species studied, where L is a poorer electron-withdrawing ligand than CO, that