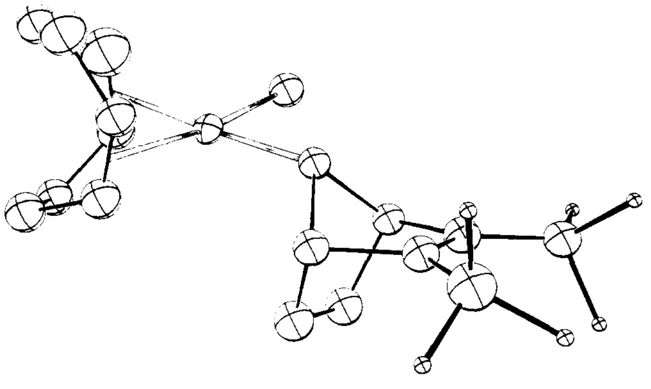
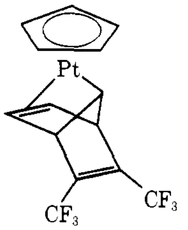


Figure 1. ORTEP illustration of the structure VIa. (Fluorine atom ellipsoids have been reduced in size for the sake of clarity.)

Interestingly, reaction of IV with carbon monoxide gives $Pt(\eta^5\text{-}C_5H_5)(CH_3)(CO)$ as a volatile, mobile yellow liquid[3] whose properties will be described more fully elsewhere. This reaction presumably proceeds via initial formation of a five-coordinate carbonyl adduct followed by $\eta^1$-Cp → $\eta^5$-Cp conversion. This demonstrates the ability of IV to form five-coordinate adducts with small molecules.

As stated above V undergoes a Diels–Alder reaction with $CF_3C{\equiv}CCF_3$ to form a norbornadiene unit. However, major rearrangement occurs in the formation of VII: one Cp changes from $\eta^1$ to $\eta^5$, the COD is displaced, and the norbornadiene is bidentate as shown.

The presence of the $\eta^5\text{-}C_5H_5$ is easily confirmed by the $J(^{195}Pt\text{-}^1H)$ coupling constant of 15.5 Hz.[4] The vinyl protons of the norbornadiene unit in VII are shifted upfield to $\tau$ 5.7 and coupled to platinum, $J(^{195}Pt\text{-}^1H) = 80$ Hz, while in VI these protons appear at $\tau$ 3.14 and are not coupled to platinum. This is consistent with the olefin being bonded to platinum in VII as shown. Significantly, a coupling constant between the platinum atom and the fluorine atoms of 14.1 Hz is observed in VII, very similar to the value observed in VI. These long range coupling constants (five bonds) are probably due to the rigid cage structure of the norbornadiene units. We conclude that cycloaddition has occurred on the Cp ring on the opposite side to platinum.



VII

It is notable that VII has a norbornadiene-metal configuration corresponding to structure VIb and is the exo analog of III. The possibility that $Pt(\eta^1\text{-}C_5H_5)_2COD$ is a precursor to $Pt(\eta^5\text{-}C_5H_5)_2$ is under investigation.

**Acknowledgments.** The financial support of the National Research Council of Canada and the award of an NRCC Postdoctorate Fellowship (to A.S.) are gratefully acknowledged.

**Supplementary Material Available.** A listing of atomic positional and thermal parameters and structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-3555.

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(6) Crystals are monoclinic, space group $P2_1/n$, $a = 23.63$ (1) Å, $b = 8.354$ (4) Å, $c = 8.935$ (4) Å, $\beta = 93.20$ (1)°, and $Z = 4$. A total of 1483 independent ($I > 3\sigma(I)$) observations were collected by diffractometric techniques. The structure, solved by the heavy atom method, has been refined by full-matrix least-squares techniques to a value of $R_1 = 9.5\%$. Further refinement is underway and the results will be reported elsewhere.

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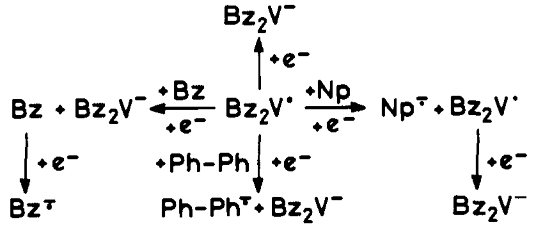
## Bis($\eta$-benzene)vanadium(−I) Anion[1]

*Sir:*

Negatively charged sandwich complexes hitherto reported in the literature are very limited in number. To our knowledge, synthesis and X-ray structural analysis of bis($\eta$-cyclooctatetraenyl)lanthanide(III) complexes, such as $[(\eta\text{-}C_8H_8)_2Ln]^-$ [2] and $[(\eta\text{-}C_8H_8)_2Ce]^-$,[3] electrochemical reduction of cobaltocene to yield $[(\eta\text{-}C_5H_5)_2Co^I]^-$,[4] and an investigation of the radical anion $[(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)Cr^{-I}]^-$ [5] represent the only published examples of unsubstituted anionic sandwich complexes. Particularly, it is surprising that the 18-valence-electron anion $[(\eta\text{-}C_6H_6)_2V^{-I}]^-$ has not yet been prepared, although a pronounced tendency to attain the inert-gas configuration is exhibited by vanadium in its organometallic compounds (e.g., $(\eta\text{-}C_7H_7)V(CO)_3$,[6] $(\eta\text{-}C_5H_5)V(CO)_4$,[7] $[(\eta\text{-}C_6H_6)V(CO)_4]^+$,[8] and $[V(CO)_6]^-$ [9]). In this communication, we report on the reduction of paramagnetic bis($\eta$-benzene)vanadium(0), $Bz_2V\cdot$,[10] to the diamagnetic anion $Bz_2V^-$.

When solutions of $Bz_2V\cdot$ in aprotic chelating solvents, like 1,2-dimethoxyethane (DME) or hexamethylphosphoramide (HMPA), are brought into contact with a potassium mirror, the ESR signals of $Bz_2V\cdot$ vanish, and the color of the reaction mixture turns from orange-red to blue. Brief exposure to air, followed by degassing of this mixture, leads to recovery of ca. 70% of $Bz_2V\cdot$, as estimated by ESR spectroscopy. On the other hand, almost quantitative conversion of $Bz_2V^-$ to $Bz_2V\cdot$ occurs with the use of the milder oxydizing agent benzophenone ($Ph_2CO$; cf. Chart I).

Chart I



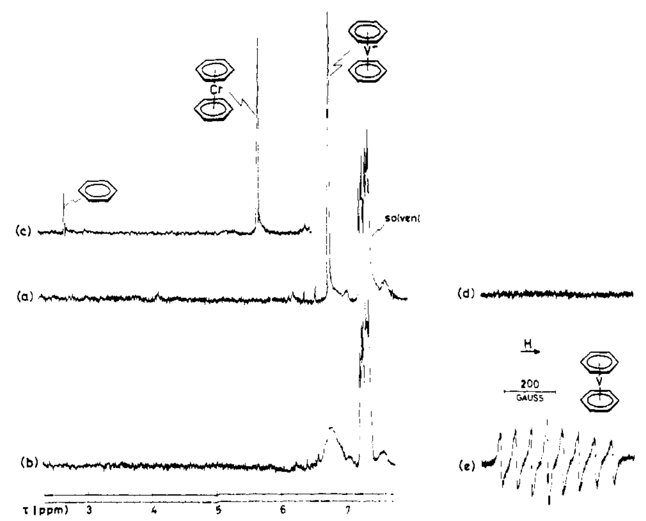


**Figure 1.** The 100-MHz $^1$H NMR spectrum (a) of $Bz_2V^-$ in HMPA-$d_{18}$ as obtained at room temperature upon exhaustive reduction with K. After standing for ca. 30 min without exposure to K, this solution of $Bz_2V^-$ gives rise to spectrum b. The NMR spectrum (c) results from $Bz_2Cr$ under conditions analogous to (a). ESR records (d and e) are taken at room temperature of the solutions exhibiting the NMR spectra a and b, respectively.

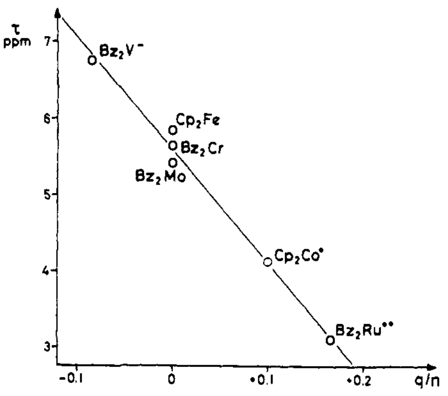


**Figure 2.** Plot of $^1$H chemical shifts, τ, vs. normalized formal charges, $q/n$, for several 18-valence-electron sandwich complexes: $Bz_2V^-$ in HMPA-$d_{18}$, this work; $Cp_2Fe$ in DMSO-$d_6$, this work; $Bz_2Mo$ in benzene-$d_6$, ref 16; $Bz_2Cr$ in HMPA-$d_{18}$, this work; $Cp_2Co^+$ in DMSO-$d_6$, ref 17; $Bz_2Ru^{2+}$ in DMSO-$d_6$, ref 18.

Figure 1a shows the $^1$H NMR spectrum obtained upon exhaustive reduction of $Bz_2V\cdot$ with K in HMPA-$d_{18}$. It displays a sharp signal at τ 6.72 which is consistent with the structure of an axially symmetric anion $[Bz_2V^{-I}]^-$, in analogy with the corresponding absorption of the isoelectronic chromium complex $Bz_2Cr^0$ (τ 5.64; Figure 1c). Under the conditions of our experiment, the radical $Bz_2V\cdot$ slowly reforms when the solution of $Bz_2V^-$ in HMPA-$d_{18}$ is allowed to stand void of further contact with potassium. A concomitant buildup of the ESR spectrum due to $Bz_2V\cdot$ (Figure 1e) and a gradual broadening of the NMR signal are observed (Figure 1b). The fast electron exchange between $Bz_2V^-$ and $Bz_2V\cdot$, as evidenced by such broadening,[11,12] corroborates our assignment of the NMR signal at τ 6.72 to the anion $Bz_2V^-$.

In order to assess the electron affinity of $Bz_2V\cdot$, the complex was reduced in presence of equimolar amounts of naphthalene (Np), biphenyl (Ph-Ph) or benzene (Bz), respectively, the formation of the anions $Bz_2V^-$, $Np\cdot^-$, $Ph\text{-}Ph\cdot^-$ and $Bz\cdot^-$ being monitored by ESR spectroscopy. The result of these experiments (Chart I) point to a sequence, $Np > Bz_2V\cdot \approx Ph\text{-}Ph > Bz$, of decreasing electron affinity. The ready uptake of an additional electron by $Bz_2V\cdot$, as contrasted with the behavior of $Bz_2Cr$,[13] may be rationalized by the different nature of the frontier orbitals involved. Whereas reduction of $Bz_2V\cdot$ to $Bz_2V^-$ introduces a second electron into a quasi-*nonbonding* orbital (an almost pure metal $d_{z^2}$-AO $a_{1g}$),[14] the formation of $Bz_2Cr\cdot^-$ from $Bz_2Cr$ would lead to the single occupancy of an *antibonding* orbital (presumably an MO $e_{2u}$ with a dominant π-ligand character).[5] That this simple one-electron model must be considered an over-simplification[15] is indicated by the plot of proton chemical shifts, τ vs. formal charges $q/n$ (normalized according to the number $n$ of ring protons). The slope of the line for several 18-valence-electron sandwich complexes (Figure 2) amounts to ca. +15 ppm per unit charge, thus being enhanced by a factor 1.5 relative to the uncoordinated cyclic π-systems.[19] This result is not anticipated by a naive orbital picture in which charge differences between the complexes would exclusively concern the central atom. Also rather unexpected is the high degree of correlation (Figure 2) if one bears in mind that the metals in the individual compounds belong to different transition series.[20]

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(12) In contrast to the signal of $Bz_2V^-$, there is essentially no broadening of the residual absorption due to the isotopic impurities in HMPA-$d_{18}$ (Figure 1b).

(13) $Bz_2Cr$ undergoes no reduction when allowed to react with solvated electrons produced by K in DME at −80°.[5] On the other hand, upon prolonged exposure of $Bz_2Cr$ to a potassium mirror in HMPA-$d_{18}$ at room temperature, a gradual cleavage of the complex must occur, since the $^1$H NMR signal of free benzene is observed along with that of unreacted compound $Bz_2Cr$ (Figure 1c).

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## Acyl- and Amino-Transfer Routes in Pepsin-Catalyzed Reactions

*Sir:*

For many years, it has been accepted that the pepsin-catalyzed hydrolysis of oligopeptide substrates, of the general type X-CO-NH-Y, involves the formation of a so-called "amino-enzyme" (enzyme-NH-Y or its noncovalent equivalent, enzyme:$^+NH_3$-Y), with the ordered release of the two halves of the substrate: X-COO$^-$ then $^+NH_3$-Y.[1] This view has been based upon studies of the pepsin-catalyzed