um Research Fund, administered by the American Chemical Society.

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(11) Solid samples of the PF_6^- and BPh_4^- salts of $[Rh(CNPh)_4]^+$ exhibit a single $\nu(C{\equiv}N)$ ir absorption at 2150 cm^{-1}. A yellow CH_2Cl_2 solution of the PF_6^- salt, which contains monomeric $[Rh(CNPh)_4]^+$, has $\nu(C{\equiv}N)$ at 2160 cm^{-1}. Concentrated blue solutions of the PF_6^- salt in acetonitrile also display a single $\nu(C{\equiv}N)$ band at 2160 cm^{-1}. Neither the solids nor concentrated acetonitrile solutions exhibit any ir absorptions attributable to bridging isocyanides.

(12) According to simple Hückel theory, the dimer (E_D) and trimer (E_T) transition energies are given by: $E_D = E_M + \beta$; $E_T = E_M + \sqrt{\beta}$; $E_M = E(a_{1g} \rightarrow a_{2u})$ in the monomer, and $\beta = \beta_{a_{1g}} + \beta_{a_{2u}}$. Taking $\beta = 7100\ cm^{-1}$, we calculate $E_D = 17{,}200\ cm^{-1}$ and $E_T = 14{,}300\ cm^{-1}$. For comparison, the experimental values are 17,600 and 13,800 cm^{-1}, respectively.

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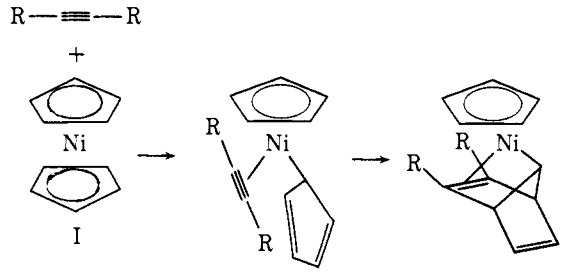
Diels-Alder Reactions of Monohaptocyclopentadienyl Complexes of Platinum

Sir:

Many examples of cycloaddition reactions between cyclic polyolefins coordinated to transition metals and electrophilic acetylenes are known.[1] In many of these the metal is thought to play a crucial role. "Symmetry forbidden" thermal cycloadditions have been attributed[1a] to the lifting of symmetry constraints by the metal. In "allowed" reactions metal participation may induce a template effect which overcomes large negative entropy factors by binding both reactants in close proximity and in the proper orientation for reaction. Alternatively, just one species may be activated by coordination to the metal.

Diels-Alder addition of electrophilic acetylenes to nickelocene was one of the first such cycloadditions reported.[1b]



I II III

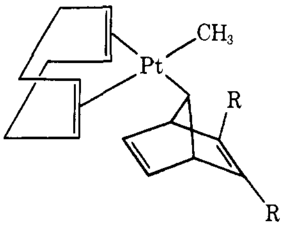
$R = CF_3, COOCH_3$

III results from the ($2\pi + 4\pi$) addition of the acetylene to the cyclopentadienyl (Cp) ring. Addition occurs from the same side of the ring as the nickel atom such that the double bond formed from the acetylene is bonded to the metal. This has led to the postulate that II may be an intermediate[2] resulting from prior acetylene coordination to the metal.

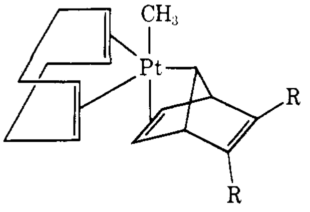
We have prepared two new platinum(II) species, $Pt(\eta^1\text{-}C_5H_5)(CH_3)(COD)$ (IV) and $Pt(\eta^1\text{-}C_5H_5)_2(COD)$ (V), where COD = 1,5-cyclooctadiene. The stereochemistry of the Diels-Alder reactions of the monohapto Cp rings in these compounds is of interest, since square planar platinum(II) complexes are often capable of forming five-coordinate adducts with acetylenes.

Reaction of $PtCl(CH_3)(COD)$ and $PtCl_2(COD)$ with C_5H_5Tl in THF yields IV and V, respectively.[3] The cyclopentadienyl protons appear as a sharp peak in both NMR spectra at about τ 4 with a ^{195}Pt coupling constant of approximately 40 Hz characteristic of the monohapto bonding mode.[4] Observation of ^{195}Pt-H coupling to the protons of the vinyl groups establishes that the COD is bidentate in both cases. Cooling a NMR sample of IV to −90° does not cause any broadening of the Cp resonance which is consistent with rapid ring "whizzing"[5] at this temperature. Treatment of IV and V with $CF_3C{\equiv}CCF_3$ results in the formation of Diels-Alder adducts VI and VII, respectively.[3] The presence of a norbornadiene residue in each of VI and VII was easily detected by means of its characteristic ^1H spectrum.[1b]

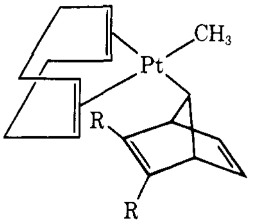
For IV a ($2\pi + 4\pi$) reaction between the η^1-Cp metal species and an acetylene could lead to four possible products, VIa-d. VIa and VIb result from acetylene attack on the η^1-Cp ring from the side opposite the metal, while VIc and VId result from attack on the ring from the same side as the metal. Interconversion of VIa with VIc or VIb with VId requires inversion at the apical carbon which is σ-bonded to the metal, a high energy process which must be considered unlikely to occur.



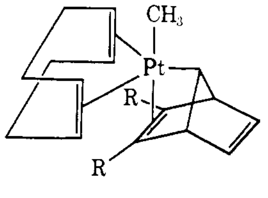
VIa



VIb



VIc



VId

$R = CF_3$

The observed coupling for VI between the ^{195}Pt and ^{19}F atoms of 12 Hz was sufficiently small that it could be interpreted as arising from a direct bonding interaction (VId), a long range coupling (VIa or VIb), or a through space coupling (VIc). An X-ray structure determination was undertaken;[6] see paragraph at end of paper regarding supplementary material. The structure found, shown in Figure 1, is that of VIa, and results from the addition of C_4F_6 to the ring on the side opposite the platinum atom substituent. This implies *no* metal participation via a template or activation mechanism and *no* precoordination of the attacking molecule of C_4F_6 as has been suggested for nickel and other systems.

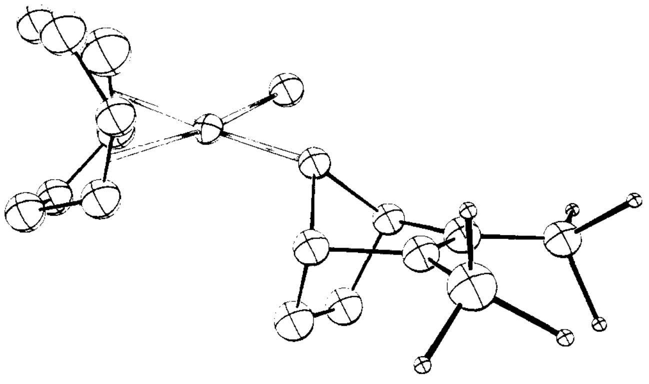
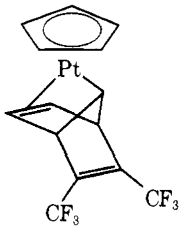


Figure 1. ORTEP illustration of the structure VIa. (Fluorine atom ellipsoids have been reduced in size for the sake of clarity.)

Interestingly, reaction of IV with carbon monoxide gives Pt(η^5-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 η^1-Cp → η^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 η^1 to η^5, the COD is displaced, and the norbornadiene is bidentate as shown.

The presence of the η^5-C_5H_5 is easily confirmed by the $J(^{195}\text{Pt}-^1\text{H})$ coupling constant of 15.5 Hz.[4] The vinyl protons of the norbornadiene unit in VII are shifted upfield to τ 5.7 and coupled to platinum, $J(^{195}\text{Pt}-^1\text{H}) = 80$ Hz, while in VI these protons appear at τ 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(η^1-C_5H_5)$_2$COD is a precursor to Pt(η^5-C_5H_5)$_2$ is under investigation.

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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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Bis(η-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(η-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(η-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