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(15) Attempts to isolate a burgundy samarium complex have been unsuccessful. Precipitation with hexane or removal of THF causes the resulting solid to revert to a yellow color.

(16) Color changes in THF solutions have also been observed for some other Cp_2LnR complexes, but no general trends with regard to ligands can be discerned.

(17) It is, of course, possible that this band in the Er spectrum is a new band, and coincidentally absorbs at the same place as the weak band already present.

(18) Work done in partial requirement for the Ph.D. degree at TAMU.

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Received December 4, 1974

Hydridotrichlorostannatocarbonylbis(triphenylphosphine)platinum(II), $PtH(SnCl_3)(CO)(PPh_3)_2$, as a Selective Hydroformylation Catalyst

Sir:

There are relatively few literature references to the use of platinum complexes as hydroformylation catalysts, and these few appear only in the patent literature[1-3] and none of them are hydrido complexes. We have prepared the new complex, $PtH(SnCl_3)(CO)(PPh_3)_2$ (**1**) and have found that it is an active catalyst for the hydroformylation of 1-pentene at 100° and 3000 psi of synthesis gas ($CO-H_2$ = 1:1). Analysis of the aldehydes in the product showed more than 95% of the straight chain compound, hexanal. The crystalline catalyst can be recovered unchanged from the reaction mixture and may be reused without any loss of activity.

Other platinum(II) hydrides that are converted to the carbonyl complex under the reaction conditions may be used as catalysts. Thus *trans*-$[PtH(SnCl_3)(PPh_3)_2]$ (**2**) or *trans*-$[PtHCl(PPh_3)_2]$ (**3**), to which excess $SnCl_2 \cdot 2H_2O$ (mole ratio 1:5) is added, also function as effective catalysts, and **1** can be recovered from the reaction mixtures.

The reported method[4] for the preparation of **2** was modified. To a stirred solution of *trans*-$[PtHCl(PPh_3)_2]$[5] (0.76 g), benzene (25 ml), and ether (75 ml) was added 1.2 g $SnCl_2 \cdot 2H_2O$. After stirring the mixture for 30 min, the orange-yellow precipitate of **2** was filtered and washed with ether, yield 0.76 g.

A suspension of 5 g of **2** in 250 ml of benzene was placed in a 300-ml autoclave. After the autoclave was flushed three times with N_2 (1000 psi) and once with CO (1000 psi), the autoclave was charged with CO (1500 psi) and with H_2 (1500 psi), and the mixture was heated at 100°. After 6 hr, the autoclave was cooled and depressured, whereupon greenish yellow crystals separated from the solution. These crystals were filtered and washed with benzene and then with pentane: yield 4.1 g; mp 93–95° dec; ir $\nu_{(Pt-H)}$ 2165 cm^{-1}, $\nu_{(C\equiv O)}$ 2050 cm^{-1}, $\nu_{(Sn-Cl)}$ 335, 314, 292 cm^{-1} (Nujol mull). Anal. Calcd: C, 45.6; H, 3.2; Cl, 10.9. Found: C, 45.4; H, 3.2; Cl, 10.5.

At the present time, we are unsure of the exact structure of the relatively unstable complex, **1**. It may be a four-coordinate ionic salt, $[Pt(H)(CO)(PPh_3)_2]^+SnCl_3^-$, analogous to the corresponding known[6] BPh_4^- salt, or it may be a five-coordinate compound, in which case it would be quite unusual. On drying under vacuum, or on exposure to air for several days, it loses CO and gives *trans*-$[PtH(SnCl_3)(PPh_3)_2]$. Attempts to recrystallize the carbonyl complex resulted in the formation of *trans*-$[PtHCl(PPh_3)_2]$ with extrusion of CO and $SnCl_2$.

A typical hydroformylation reaction was performed as follows. $PtH(SnCl_3)(CO)(PPh_3)_2$ (2.4 g, 2.5 mmol) and 150 ml of benzene were charged into a 300-ml autoclave which was equipped with an equalizing pressure addition vessel containing 1-pentene (17.5 g, 250 mmol). After the autoclave was sealed and flushed with N_2 and CO, H_2 (1500 psi) and CO (1500 psi) were charged, and the solution was heated to 100° with stirring. 1-Pentene was then added to the autoclave and the reaction mixture stirred with heating for 2.5 hr. The product was analyzed by GLC; essentially all the olefin had disappeared and the aldehyde product consisted of 95% hexanal and 5% 2-methylpentanal.

Essentially similar results were obtained when complexes **2** or **3** (to which was added $SnCl_2 \cdot 2H_2O$) were employed as catalysts.

The rate of the reaction catalyzed by **1** is about five times that of a $Co_2(CO)_8$-catalyzed reaction carried out under the same conditions. Although a $Co_2(CO)_6(PR_3)$ catalyst[7] also leads to relatively high selectivity to straight-chain product, the rate of hydroformylation with this catalyst is negligible at 100°. $Rh(Cl)(CO)(PPh_3)_2$ or other modified Rh catalysts operate effectively at 100°, but the ratio of straight- to branched-chain aldehydes[8] is usually about 3 compared to a ratio of about 20 with the Pt catalyst, **1**.

Acknowledgments. We wish to acknowledge the partial financial support from the Hoke S. Greene Fund and the Sohio Company. Englehard Industries furnished a generous supply of platinum.

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Received February 24, 1975

Characterization of Oligomers of Tetrakis(phenyl isocyanide)rhodium(I) in Acetonitrile Solution

Sir:

There has been considerable recent interest in the optical spectra and electrical conductivities of platinum compounds in which direct metal–metal interactions are present.[1-6] Perhaps the best known examples are the double salts, such as $[Pt(NH_3)_4][PtCl_4]$ (Magnus' green salt or MGS).[1] Low solubility of the double salts has generally restricted study to solid samples, although it should be noted that Isci and Mason have obtained electronic spectra for certain $[Pt(CNR)_4][Pt(CN)_4]$ complexes in ethanol solution.[6]

Many simple platinum salts also possess unusual properties.[2,3] The planar ions in these compounds, as in MGS, stack face-to-face in infinite columns. However, with the exception of one or two mixed-valence aggregates, notably $[Pt(C_2O_4)_2]_n^{1.6n-}$, complete dissociation to monomeric fragments occurs in solution. Even the copper-colored, mixed-valence Krogmann's salt, $K_2Pt(CN)_4Cl_{0.3} \cdots 3H_2O$,

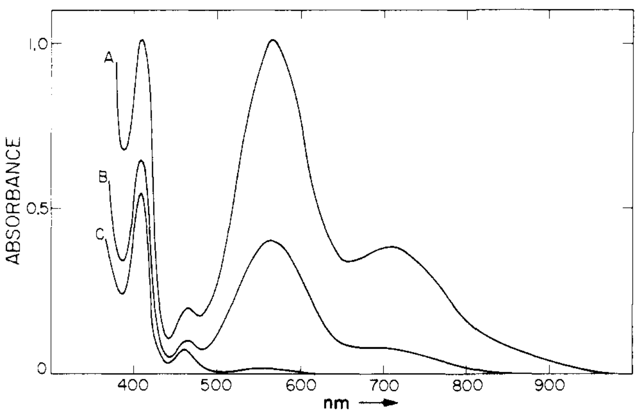

Figure 1. Electronic absorption spectra of $[Rh(CNPh)_4](PF_6)$ in acetonitrile solution at 25° (cell pathlength): A, 5.7×10^{-2} *M* (0.06 mm); B, 2.7×10^{-2} *M* (0.06 mm); C, 6.3×10^{-4} *M* (0.75 mm). The peak positions and concentration dependences for the BPh_4^- and BF_4^- salts are the same.

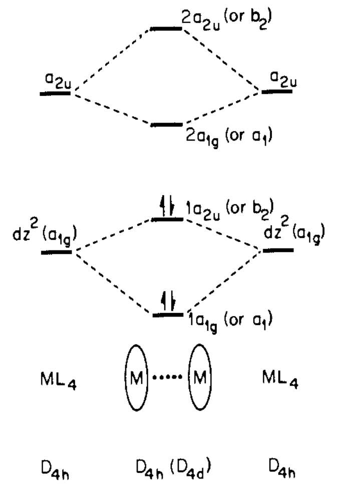

Figure 2. Relative energies of the molecular orbitals derived from $a_{1g}(d_{z^2})$ and a_{2u} monomer functions in D_{4h} (or D_{4d}) $[Rh(CNPh)_4]_2^{2+}$.

forms a nearly colorless solution containing discrete Pt(II) and Pt(IV) complex ions.[2]

We have begun a systematic investigation of metal (d^8)-metal (d^8) interactions in solution. Systems that appear to be highly promising are based on planar Rh(I) and Ir(I) isocyanides. Our work to date has shown that solution oligomerization is common for these complexes, which is in accord with molecular weight measurements made by Kawakami et al. on acetonitrile solutions containing Ir(I) aryl isocyanides.[7] Here we report an electronic spectroscopic characterization of $[Rh(CNPh)_4]_n^{n+}$ ($n = 1, 2, 3$) in acetonitrile solution.

Tetrakis(phenyl isocyanide)rhodium(I) chloride was obtained as a dark green powder from the reaction of excess phenyl isocyanide with $Rh(CO)Cl(PPh_3)_2$ or $[RhCl(COD)]_2$ in benzene solution.[8] It was converted to the crystalline, yellow PF_6^-, blue BPh_4^-, and yellow-brown BF_4^- salts by metathesis in water. For all three salts, dilute acetonitrile solutions are yellow and concentrated ones are blue. Representative absorption spectra for three different concentrations of $[Rh(CNPh)_4](PF_6)$ in acetonitrile solution are shown in Figure 1. The bands at 361, 411, 468 nm dominate the low-concentration spectra and are logically due to monomeric $[Rh(CNPh)_4]^+$. In support of this assignment, it may be noted that very similar bands have been observed in several square planar Rh(I) complexes containing π-acceptor ligands.[9,10] As the total Rh(I) concentration is increased, two new bands grow in, first at 568, then at 727 nm, while the higher energy bands decrease in relative intensity. This behavior is interpreted in terms of the following equilibria.

$$2[Rh(CNPh)_4]^+ \overset{K_1}{\rightleftharpoons} [Rh(CNPh)_4]_2^{2+}$$

$$[Rh(CNPh)_4]_2^{2+} + [Rh(CNPh)_4]^+ \overset{K_2}{\rightleftharpoons} [Rh(CNPh)_4]_3^{3+}$$

$$[Rh(CNPh)_4]_n^{n+} + [Rh(CNPh)_4]^+ \overset{K_n}{\rightleftharpoons} [Rh(CNPh)_4]_{n+1}^{(n+1)+}$$

In this scheme the 568-nm band is assigned to the dimer, as $(A_{411})^2$ vs. A_{568} yields a straight line. Further, it is reasonable to assume that the 727-nm band is attributable primarily to trimer absorption. The fact that $(A_{411})^3$ vs. A_{750} deviates slightly from linearity at very high Rh(I) concentrations suggests that higher oligomers also absorb in the same region. Using a weighted least-squares procedure to fit the data to the appropriate equations, we have computed the following equilibrium constants and molar extinction coefficients.

$$K_1(25°) = 16 \pm 1\ M^{-1} \quad \epsilon_1(411) = 6{,}000 \pm 100 \text{ monomer}$$

$$K_2(25°) = 16 \pm 3\ M^{-1} \quad \epsilon_2(568) = 14{,}800 \pm 800 \text{ dimer}$$

$$\epsilon_3(750) = 16{,}000 \pm 8{,}000 \text{ trimer}$$

The absorbances at 411, 568, and 750 nm were used to avoid overlapping peaks.

The electronic spectral properties of $[Rh(CNPh)_4]_2^{2+}$ may be understood in terms of the orbital interactions diagramed in Figure 2. As infrared spectral evidence rules out the involvement of bridging isocyanides,[11] the dimer is very probably bound through direct Rh···Rh interactions. These bonding interactions apparently are substantial, as they must overcome unfavorable coulombic forces between the cationic units. The orbitals that will interact most strongly are those that extend perpendicular to the molecular plane, namely the $a_{1g}(d_{z^2})$ and $a_{2u}[p_z,\pi^*(CNPh)]$ functions. It is also important to note that a_{1g} is likely to be the HOMO, and a_{2u} the LUMO, in the monomeric units, as the 411- and 468-nm bands of $[Rh(CNPh)_4]^+$ are entirely analogous to the well-established $a_{1g} \rightarrow a_{2u}$ features $[^1A_{1g} \rightarrow A_{2u}(^1A_{2u}),\ E_u(^3A_{2u})]$ in $[Rh(CNEt)_4]^+$,[10] $[Rh(2{=}phos)_2]^+$,[9] and $[Rh(2\text{-}phos)_2]^+$.[9] Thus the 411-nm monomer band is assigned to the spin-allowed $a_{1g} \rightarrow a_{2u}$ transition.

It is not likely that there will be a significant energy difference between D_{4h} (eclipsed) and D_{4d} (staggered) rotameric configurations for the dimeric molecules, and the MO level scheme in Figure 2 gives symmetry labels for both possibilities. In both cases the upper and lower sets contain orbitals of the same symmetry, and as a result there will be considerable mixing, stabilizing the lower set ($1a_{1g}$, $1a_{2u}$, or $1a_1$, $1b_2$) and destabilizing the upper set ($2a_{1g}$, $2a_{2u}$, or $2a_1$, $2b_2$). As the lower set is filled this stabilization must be the source of the intermonomer binding forces.

Two allowed electronic transitions are predicted for the dimer, one higher ($1a_{1g} \rightarrow 2a_{2u}$ or $1a_1 \rightarrow 2b_2$) and one lower ($1a_{2u} \rightarrow 2a_{1g}$ or $1b_2 \rightarrow 2a_1$) than the $a_{1g} \rightarrow a_{2u}$ excitation in the monomer. We assign the 568-nm band in the dimer, therefore, to $1a_{2u} \rightarrow 2a_{1g}$ (or $1a_1 \rightarrow 2b_2$). A similar analysis for a trimeric molecule predicts five allowed transitions, the lowest of which ($2a_{1g} \rightarrow 2a_{2u}$) is assigned to the 727-nm band.[12] Detailed interpretations of the electronic properties of a wide variety of Rh(I) and Ir(I) isocyanide oligomers will be presented in subsequent papers.

Acknowledgment. This research was supported by the National Science Foundation and the donors of the Petroleum 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 ν(C≡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 ν(C≡N) at 2160 cm^{-1}. Concentrated blue solutions of the PF_6^- salt in acetonitrile also display a single ν(C≡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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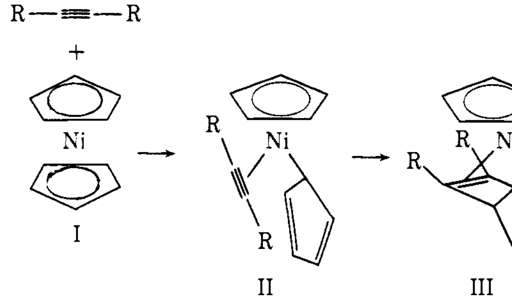
Received February 18, 1975

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]



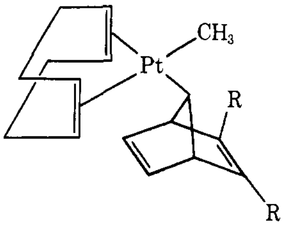
R = CF$_3$, COOCH$_3$

III results from the (2π + 4π) 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.

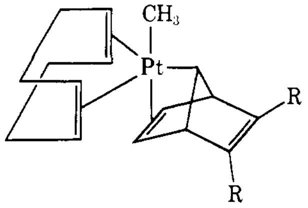
We have prepared two new platinum(II) species, Pt(η^1-C_5H_5)(CH_3)(COD) (IV) and Pt(η^1-C_5H_5)$_2$(COD) (V), where COD = 1,5-cyclooctadiene. The stereochemistry of the Diels–Alder reactions of the monohapto Cp rings in these compounds is of interest, since square planar platinum(II) complexes are often 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 ^{1}H spectrum.[1b]

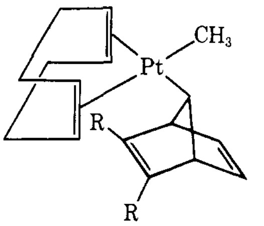
For IV a (2π + 4π) reaction between the η^1-Cp metal species and an acetylene could lead to four possible products, VIa–d. VIa and VIb result from acetylene attack on the η^1-Cp ring from the side opposite the metal, while VIc and VId result from attack on the ring from the same side as the metal. Interconversion 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.



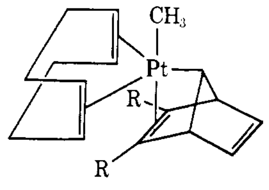
VIa



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.