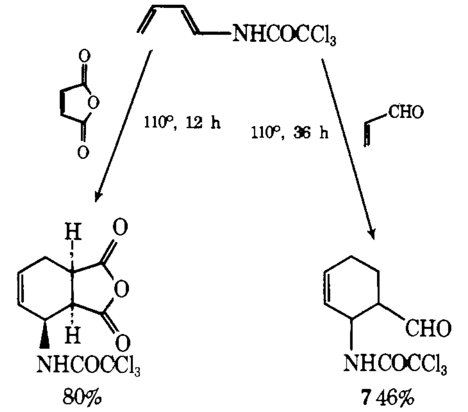
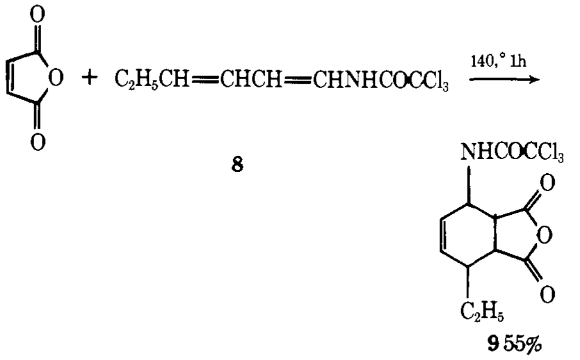
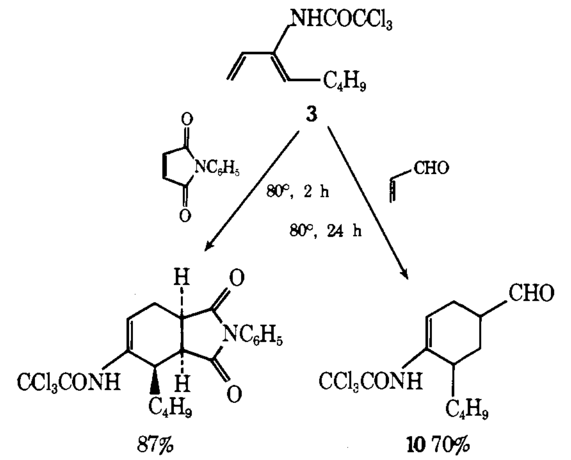


(2)



$C_2H_5CH{=}CHCH{=}CHNHCOCCl_3$

(3)



(4)

Diels-Alder reactions of trichloroacetamido-1,3-dienes as well as attempting to prepare, by similar routes, more reactive Diels-Alder 1,3-dieneamides.

Acknowledgment. We thank the National Science Foundation for support of this work under Grant No. GP-38634X and Mr. Everett R. Santee, Jr., of the University of Akron Institute of Polymer Science for assistance in obtaining the 300-MHz ^{1}H NMR spectra.

References and Notes

(1) For example, the diene volume of "Houben-Weyl" devotes only 6 pages to such dienes.[2]

(2) "Houben-Weyl", 4th ed, Vol. 5/1C, Thieme Verlag, Stuttgart, Germany, 1970, in particular pp 198–200, 513–514.

(3) Cf. S. Hunig and H. Kahanek, *Chem. Ber.*, **90**, 238 (1957); recent examples include: H. Leotte, *Rev. Port. Quim.*, **7**, 214 (1965); *Chem. Abstr.*, **65**, 13647*f* (1966); G. Satzinger, *Justus Liebigs Ann. Chem.*, **728**, 64 (1969).

(4) Reportedly prepared by acylation of 2-amino-1,3-butadiene which was formed from 2-amino-3-butyne by pyrolysis at 200–350 °C: J. B. Dickey, U.S. Patent 2 446 172 (1948); *Chem. Abstr.*, **42**, 8209*i* (1948).

(5) The 1-phthalimido- and 2-phthalimido-1,3-butadienes are known. They are prepared by multistep sequences in low overall yield from 1,3-butadiene[6] and ethyl acetoacetate,[7] respectively. Recently the synthesis of a cyclic acetamido-1,3-diene from isophorone oxime was reported.[8] An apparently general synthesis of *trans-N*-acyl-*N*-alkyl-1-amino-1,3-dienes has also recently appeared.[9]

(6) A. Terada, *Nippon Kagaku Zasshi*, **81**, 1773 (1960); A. Terada and K. Murata, *ibid.*, **83**, 490 (1962).

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(8) R. B. Boar, J. F. McGhie, M. Robinson, D. H. R. Barton, D. C. Horwell, and R. V. Stick, *J. Chem. Soc., Perkin Trans. 1*, 1237 (1975).

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(11) (a) L. E. Overman, *Tetrahedron Lett.*, 1149 (1975); (b) L. E. Overman, *J. Am. Chem. Soc.*, in press.

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(18) The yields were not significantly improved by adding up to 10% of *tert*-butylcatechol as a free radical inhibitor.

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(20) The observed magnitude (J = 9.5 Hz) of the coupling constant for the vinylic hydrogens at C-1 and C-2 was inconclusive.[21]

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(24) A colorless liquid: $C_9H_{10}Cl_3NO_2$ (MS); ^{1}H NMR (CDCl$_3$, δ) 10.03 (d, J = 0.8 Hz) and 9.97 (d, J = 1.6 Hz) (CHO), 6.8 (m, NH), 5.4–6.2 (m, C*H*=C*H*), and 4.7 (m, C*H*NHCOCCl$_3$).

(25) Preferential endo-addition is assumed.[2,13]

(26) A colorless liquid: $C_{13}H_{18}Cl_3NO_2$ (MS); ^{1}H NMR (CDCl$_3$, δ) 9.97 and 9.87 (br s, CHO), 7.6 (m, NH), and 6.17 (br t, J = 4 Hz, =CH).

(27) (a) A. P. Sloan Foundation Fellow, 1975–1977; (b) Earl C. Anthony predoctoral fellow, 1974–1975.

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Association of Isocyanide Complexes of Rhodium(I) and Rhodium(III) in Solution

Sir:

We have found that rhodium complexes of the type $(RNC)_4Rh^+$ and *trans*-$(RNC)_4RhX_2^+$ (R = alkyl; X = halide) undergo appreciable association in solution. Previously, three other types of interaction between d^8 and d^6 complexes have been recognized. (1) A number of Pt(II) and Pt(IV) complexes associate in the solid state to form columns constructed of alternating quasi-planar Pt(II) and six-coordinate Pt(IV) centers.[1] In these columns halide ligands are located between platinum atoms in the column and no direct metal-metal bonding is present. (2) A different arrangement occurs in Krogmann's salt, $K_2Pt(CN)_4Cl_{0.32}(H_2O)_{2.6}$. In this case, reaction of $Pt(CN)_4^{2-}$ with $Pt(CN)_4Cl_2^{2-}$ produces a solid which consists of stacks of $Pt(CN)_4$ units with direct platinum-platinum bonds.[2] (3) In solution the Pt(II)-catalyzed substitution reactions of Pt(IV) complexes are conventionally interpreted as involving a transient, ligand-bridged Pt(II)-Pt(IV) species.[3]

Electronic spectra, infrared spectra, and synthetic studies demonstrate the occurrence of the equilibrium shown in (1). Solutions containing both $(C_6H_{11}NC)_4Rh^+$ and *trans*-

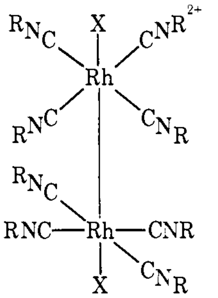
$$(RNC)_4Rh^+ + trans\text{-}(RNC)_4RhX_2^+ \rightleftarrows (RNC)_8Rh_2X_2^{2+} \quad (1)$$

$(C_6H_{11}NC)_4RhI_2^+$ have a unique electronic spectrum which differs from that expected from the sum of the spectra of $(C_6H_{11}NC)_4Rh^+$ and *trans*-$(C_6H_{11}NC)_4RhI_2^+$ [4-6] This is demonstrated in Figure 1 where the new absorption at 452 nm is readily apparent. Analysis of the spectra of various combinations of $(C_6H_{11}NC)_4Rh^+$ and *trans*-$(C_6H_{11}NC)_4RhI_2^+$ in acetonitrile solution at 25 °C has given a value of 4.7×10^3 for the equilibrium constant for reaction 1. Similar spectra have been observed in other solvents, but the magnitude of the equilibrium constant decreases as the dielectric constant of the solvent decreases (K_{eq}(solvent): 5.8×10^3 (dimethyl sulfoxide); 2.8×10^3 (nitromethane); 3.2×10^2 (acetone); no adduct could be detected in dichloromethane or chloroform solution). Similarly $(C_6H_{11}NC)_4Rh^+$ and $(C_6H_{11}NC)_4RhBr_2^+$ associate in acetonitrile to form $(C_6H_{11}NC)_8Rh_2Br_2^{2+}$ (λ_{max}, 415 nm, $K_{eq} = 2 \times 10^4$).

Reaction 1 may also be detected by infrared spectroscopy. In acetone solution $(C_6H_{11}NC)_4Rh^+$ and *trans*-$(C_6H_{11}NC)_4RhI_2^+$ have a single isocyanide stretching frequency at 2170 and 2239 cm^{-1}, respectively. A mixture of these two complexes in acetone solution exhibits, in addition to these two bands, a new absorption at 2214 cm^{-1}; no other new bands due to the adduct could be detected in the region 2400-1700 cm^{-1}

Similar spectroscopic evidence for the formation of the following other adducts in acetonitrile or acetone solution has been found: $(CH_3NC)_8Rh_2I_2^{2+}$; $(n\text{-}C_4H_9NC)_8Rh_2I_2^{2+}$; $(C_6H_5CH_2NC)_8Rh_2I_2^{2+}$; $(C_6H_{11}NC)_8Rh_2Cl_2^{2+}$. Mixtures of $(t\text{-}C_4H_9NC)_4Rh^+$ with either $(t\text{-}C_4H_9NC)_4RhI_2^+$ or $(t\text{-}C_4H_9NC)_4RhBr_2^+$ in acetonitrile or acetone give no evidence for the formation of adducts.

Favorable solubility conditions have allowed the isolation of $[(C_6H_{11}NC)_8Rh_2I_2][B(C_6H_5)_4]_2$ as red-brown crystals [Anal. Found for $C_{104}H_{128}B_2I_2N_8Rh_2$: C, 63.66; H, 6.67; N, 5.40; I, 12.45; ir (Nujol mull) 2208 cm^{-1} ν(C≡N); λ_{max} (Nujol mull) 410, 465 nm]. This solid may be isolated either from an equimolar mixture of $(C_6H_{11}NC)_4Rh^+$ and *trans*-$(C_6H_{11}NC)_4RhI_2^+$ or by oxidizing $(C_6H_{11}NC)_4Rh^+$ with 0.5 mol of iodine.



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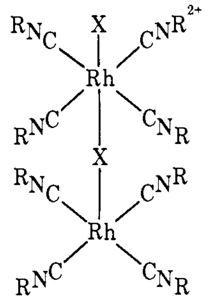

2

The two most likely structures for $(RNC)_8Rh_2X_2^{2+}$ are **1** and **2**. No electron spin resonance spectra have been detected for these adducts. The proton magnetic resonance spectra of mixtures of $(RNC)_4Rh^+$ and $(RNC)_4RhI_2^+$ indicate that the equilibrium (eq 1) is rapid on the ^1H NMR time scale; only a single averaged type of R group is observed. The infrared spectra indicate that only terminal, not bridging, isocyanide ligands are present. The observation that the electronic spectra of the adducts depend on the halide indicates that at least one halide is present as a ligand. Since there is no increase in the electrical conductivity of acetonitrile solutions of $(C_6H_{11}NC)_4Rh^+$ and $(C_6H_{11}NC)_4RhI_2^+$ after mixing, it appears that no halide is released upon adduct formation. Structure **2** is appealing since it requires little atomic motion to assemble, but it is difficult to account for the nonexistence of $(t\text{-}C_4H_9NC)_8Rh_2X_2^{2+}$ on the basis of this structure. Additionally, no affinity of $(RNC)_4Rh^+$ for free halide has been detected; consequently it is difficult to imagine that $(RNC)_4Rh^+$ would exhibit a tendency to bind to a coordinated halide of a cationic complex. If the adduct possesses structure **1** then the lack of formation of $(t\text{-}C_4H_9NC)_8Rh_2X_2^{2+}$ can be ascribed to steric interference between adjacent ligands. The observation of only a single isocyanide stretching frequency in the infrared spectrum of the adduct is also more in accord with structure **1**. For such a structure with D_{4d} symmetry two infrared active stretching frequencies with b_2 and e symmetry are expected and the e mode should be significantly more intense.[7] Structure **2** should produce four infrared active isocyanide stretching modes. These adducts are formally Rh(II) species and a number of Rh(II) complexes with direct rhodium-rhodium bonds are known.[8] However, $(RNC)_8Rh_2X_2^{2+}$ are the first Rh(II) species which show significant degrees of disproportionation in solution. We are exploring how adduct formation between Rh(I) and Rh(III) complexes bears on the mechanism of oxidative-addition, the isomerization of Rh(III) complexes, and the preparation of complexes with unusual oxidation states.

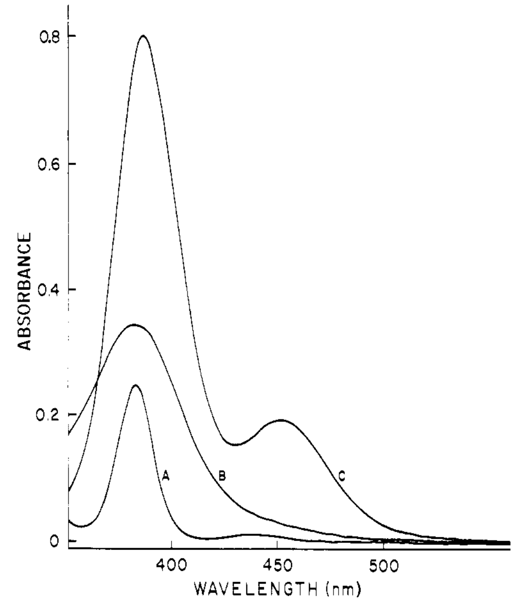

Figure 1. Electronic spectra of: A, 2.5×10^{-4} M $(C_6H_{11}NC)_4Rh^+$; B, 2.5×10^{-4} M $(C_6H_{11}NC)_4RhI_2^+$; C, 2.5×10^{-4} formal $(C_6H_{11}NC)_4Rh^+$ and 2.5×10^{-4} formal $(C_6H_{11}NC)_4RhI_2^+$ in acetonitrile solution at 25 °C with a 1-mm path length cell.

Acknowledgment. We thank Matthey Bishop, Inc. for a generous loan of rhodium.

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(4) The electronic spectrum of $(C_6H_5NC)_4Rh^+$ in acetonitrile indicates that this complex undergoes a significant degree of self-association presumably through direct rhodium–rhodium bonding.[5] Alkyl isocyanide complexes $(RNC)_4Rh^+$ also undergo self-association in acetonitrile solution. Their electronic spectra do not obey Beer's law. The growth of a new band in the visible region accompanies self-association (λ_{max} for this band is as follows; $(C_6H_{11}NC)_4Rh^+$, 512; $(n\text{-}C_4H_9NC)_4Rh^+$, 510; $(C_6H_5CH_2NC)_4Rh^+$, 517; $(CH_3NC)_4Rh^+$, 555 nm). However, apparently because of steric effects $(t\text{-}C_4H_9NC)_4Rh^+$ does not associate (and does obey Beer's law) in acetonitrile over the concentration range 0.06 to 1×10^{-5} M. The studies of association between Rh(I) and Rh(III) complexes reported here have been carried out with concentrations of $(RNC)_4Rh^+$ in which the degree of self-association is negligible.

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Coordination Geometries and Bond Types in Three-Coordinate Phosphine Complexes of Copper(I), Silver(I), and Gold(I)

Sir:

It has recently been shown that the bidentate ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (PP)[1] forms square planar complexes of the type $[MX_2(PP)]$ (M = Ni(II), Pd(II), and Pt(II), X = halide ion) in which the two phosphorus atoms span trans positions.[2] We report here the syntheses of complexes [MCl(PP)] (M = Cu(I), Ag(I), and Au(I)) and discuss their conductivities in solution in terms of their molecular geometries obtained from crystal structure determinations.

The complex [CuCl(PP)] was prepared by mixing acetone solutions of PP and $CuCl_2{\cdot}6H_2O$. The corresponding silver and gold complexes were obtained similarly starting from AgCl and $[AuCl(Ph_3P)]$, respectively. Pure crystals suitable for x-ray diffraction, were obtained by slow crystallization from benzonitrile (Cu and Au) and acetonitrile (Ag).

The structures of [CuCl(PP)]·PhCN, [AgCl(PP)], and [AuCl(PP)] have been determined from three-dimensional diffractometer data and refined to conventional *R* values of 7.4, 4.5, and 3.8%, respectively. The important parameters describing the coordination geometries are summarized in Table I. The metal atoms are coordinated to two phosphorus atoms and one chlorine atom. The deviations of M from the plane of the ligands are 0.012 Å (Cu), 0.066 Å (Ag), and 0.040 Å (Au).

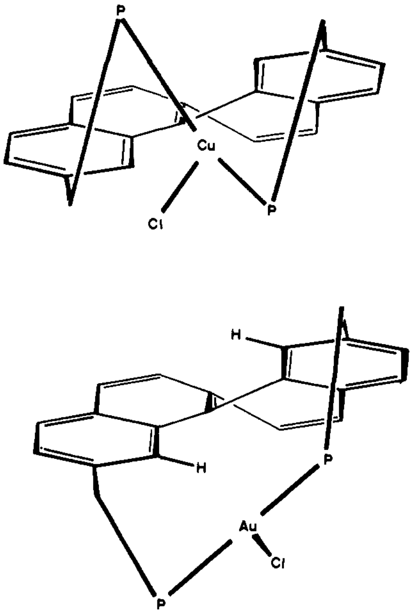

Figure 1. Schematic drawing of ligand conformations projected along the approximate twofold axis of the benzo[*c*]phenanthrene skeleton.

The most striking feature of this set of structures is the change in P_1MP_2 bond angles which increase from 132° (Cu) to 141° (Ag) to 176° (Au). Thus, in the latter compound the donor atom geometry is practically T-shaped. The observed M-Cl bond lengths are all shorter than the corresponding sums of the ionic radii[3] (by 0.55 Å (Cu), 0.56 Å (Ag), and 0.36 Å (Au)), but they exceed the standard distances obtained by adding the covalent radius of chlorine[3] and the single-bond radii of the metals[6] (by 0.06 Å (Cu), 0.19 Å (Ag), and 0.49 Å (Au)). At the same time the average M-P distances become shorter than the corresponding sum of reference radii (by 0.04 Å (Cu), 0.01 Å (Ag), and 0.13 Å (Au)). Thus, the lengthening and weakening of the M-Cl bonds are compensated by a shortening and strengthening of the M-P bonds made possible, in part, by the concomitant opening of the P-M-P angles. This correlation of changes in bond lengths and angles may be used as a model of the minimum energy pathway[4] that leads from three-coordinate to two-coordinate complexes, or of the reverse process.

The ligand PP occurs in two different conformations, in the copper and silver complexes the $-CH_2PPh_2$ groups point in opposite directions while in the free ligand[5] and in the gold complex they point in the same direction (see Figure 1).

The complexes [MCl(PP)] represent the first complete set of compounds of Cu(I), Ag(I), and Au(I), of the type $[MXL_2]$ (L = tertiary phosphine), for which structural data have been obtained as no crystal structure determination of mononuclear complexes $[AgX(R_3P)_2]$ appears to have been reported.

Comparison of structural data for $[CuBr(Ph_3P)_2]$[6] ($Cu-P_1$ = 2.282 (3) Å, $Cu-P_2$ = 2.263 (3) Å, P_1-Cu-P_2 = 126.0 (1) Å) and for the PP complex shows that the donor atom geometries in the two complexes are very similar. On the other hand, the P_1-Au-P_2 bond angle in [AuCl(PP)] differs considerably from that found in $[AuCl(Ph_3P)_2]$[7] ($Au-P_1$ = 2.323 (4) Å, $Au-P_2$ = 2.339 (4) Å, P_1-Au-P_2 = 132.1 (1) °). A direct inference from these comparisons is that while the ligand PP can adopt coordination geometries similar to those of the corresponding complexes with monodentate tertiary phosphines, its steric requirements are such that it imparts some preference for linear P-M-P bonds and thus it provides a useful probe for assessing the relative tendencies of metal ions to form trigonal vs. digonal complexes.

The different nature of the M-Cl bonds in the [MCl(PP)] complexes is also reflected by their molar conductances. These were determined in nitromethane and acetonitrile over a range of concentrations[8] and some of the data are given in Table I.

Table I. Molar Conductances (in $ohm^{-1}\ cm^2\ mol^{-1}$ for 10^{-3} M solutions at 25°) and Coordination Geometries (with esd's) for Complexes [MCl(PP)]

M	$\Lambda(CH_3NO_2)^a$	$\Lambda(CH_3CN)^a$	$d(P_1-M)$	$d(P_2-M)$	d(M-Cl), Å	$\alpha(P_1MP_2)$	$\alpha(P_1MCl)$	$\alpha(P_2MCl)$, deg
Cu	7.2	insol.	2.258(2)	2.217(4)	2.222(2)	131.9(1)	104.8(1)	123.3(1)
Ag	18.3	18.6	2.458(3)	2.411(3)	2.514(4)	140.7(1)	98.2(1)	120.9(1)
Au	65.5	83.0	2.307(2)	2.310(2)	2.818(3)	175.7(1)	90.4(1)	93.4(1)

[a] Values quoted for solutions of 1:1 electrolytes range from 75 to 95 $ohm^{-1}\ cm^2\ mol^{-1}$ in CH_3NO_2 and from 120 to 160 $ohm^{-1}\ cm^2\ mol^{-1}$ in CH_3CN.[9]