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Preliminary communication

AN UNUSUAL OXIDATIVE ADDITION-LIGAND ELIMINATION REACTION. PREPARATION AND STRUCTURE OF $RhCl_2(PMe_2Ph)_2(C_3Ph_3)$

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Summary

The *sym*-triphenylcyclopropenium cation ($C_3Ph_3^+$) stabilized as the Cl^- or PF_6^- salt, undergoes facile reactions at room temperature with *trans*-$Rh(CO)Cl(PMe_2Ph)_2$ to produce complexes which result from the oxidative cleavage of the ring and decarbonylation of the organometallic reactant. The product of the $C_3Ph_3^+Cl^-$ reaction has been fully characterized by X-ray analysis and is shown to be $RhCl_2(PMe_2Ph)_2(C_3Ph_3)$.

Oxidative addition reactions to square planar d^8 rhodium(I) and iridium(I) complexes of the Vaska type, *trans*-$M(CO)Cl(PR_3)_2$, have been well studied [1, 2] and, under most experimental conditions, simply proceed to add substrate to produce an octahedral metal(III) complex. In other cases, e.g. in $M(PPh_3)_4$ [3] (M = Pd, Pt) where steric crowding is severe or in $Ir(N_2)Cl(PR_3)_2$ [4] or $(PPh_3)_2Pt(C_2H_4)$ [3, 5] where metal—ligand bonding is weak, ligand elimination reactions occur prior to or concurrent with the oxidative addition reactions.

The combination of the oxidative addition and ligand elimination reactions is a common mode of chemical reactivity of many homogeneous catalysts [1, 6]. However, in the case of homogeneous catalysts of the Vaska-type, *trans*-$M(CO)X(PR_3)_2$ (M = Rh, Ir, X = halide, R = alkyl or aryl), the complexes smoothly undergo oxidative addition without loss of ligand [7]. In this communication we wish to present some of our initial synthetic findings, including preliminary X-ray diffraction results, on the reactions of d^8 rhodium(I) complexes of the type *trans*-$Rh(CO)Cl(PR_3)_2$ with the strained cyclic triphenylcyclopropenium ion $C_3Ph_3^+X^-$ where, in the case $R_3 = Me_2Ph$, we have observed facile loss of carbon monoxide at room temperature. These results will be compared to work previously reported by Weaver and co-workers [8] on analogous iridium complexes where no CO loss is noted.

Stoichiometric quantities of $Rh(CO)Cl(PMe_2Ph)_2$ and C_3Ph_3Cl were stirred in CH_2Cl_2 under an inert atmosphere (N_2) for approximately one hour. Carbon monoxide was evolved and the color of the solution went from yellow to deep blue-green. The solvent was reduced and a green-black microcrystalline material was obtained upon cooling at 0°C overnight. Crystals suitable for microanalysis and X-ray diffraction work were grown by the Soxhlet-extraction technique from methylene chloride. Since preliminary spectroscopic and micro-analytical data were insufficient to reveal the structural nature of the C_3Ph_3 moiety, a single crystal X-ray diffraction study was initiated.

The results of the X-ray analysis*, shown in Fig. 1, indicate that the Rh(CO)Cl$(PMe_2Ph)_2$ complex in the presence of $C_3Ph_3^+Cl^-$ has undergone an oxidative addition reaction similar to that observed for $Ir(CO)Cl(PMe_3)_2$ [8] with the exception that the carbonyl ligand has been eliminated and replaced by chloride. The rhodium(I) complex has oxidatively cleaved the C—C bond of the cyclopropenium cation to generate a bidentate propenyl ligand which chelates *cis*-positions in the pseudooctahedral rhodium(III) adduct. The PMe_2Ph ligands retain their *trans* relationship while the chlorines are disposed *cis* to each other and *trans* to the propenyl group carbon atoms. Crystallographically the molecule possesses two-fold symmetry with the axis bisecting the Cl—Rh—Cl' angle and passing through Rh, C(2), C(21), and C(24); the independent unit consists of half of the $RhCl_2(PMe_2Ph)_2(C_3Ph_3)$ molecule.

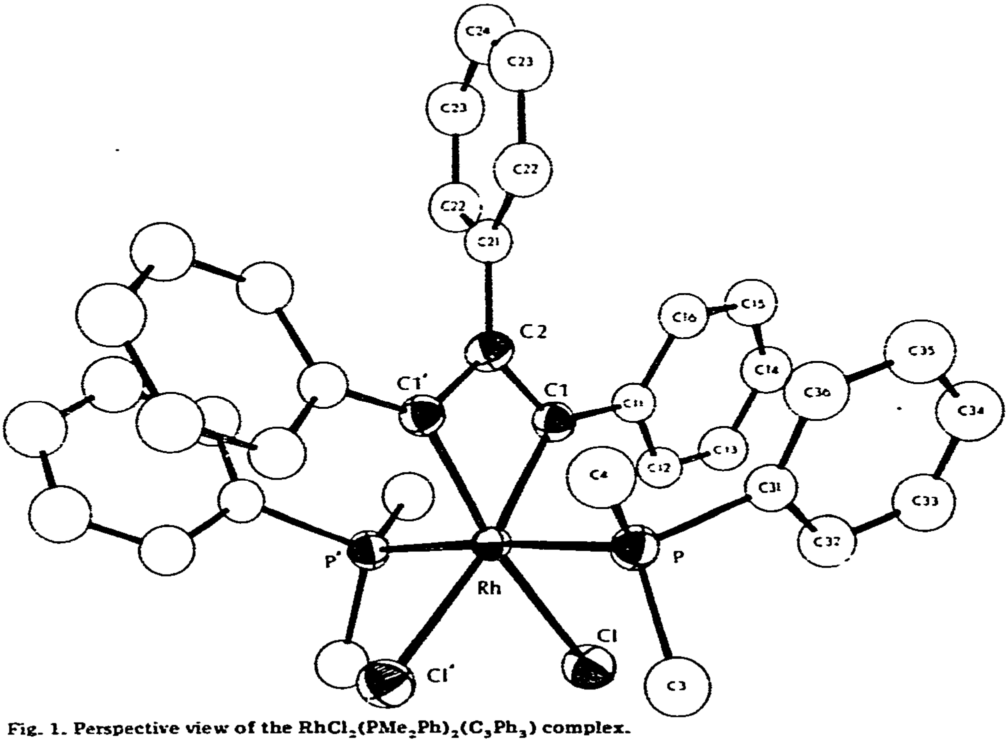

Fig. 1. Perspective view of the $RhCl_2(PMe_2Ph)_2(C_3Ph_3)$ complex.

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[*] $[RhCl_2(PMe_2Ph)_2(C_3Ph_3)]$: Monoclinic; $C2/c$; unit cell parameters are a 19.190(7), b 11.892(6), c 14.346(4) Å, β 93.88(2)°, V 3266(1) $Å^3$; ρ_{obsd} 1.45 vs. ρ_{calc} 1.46 g cm^{-3} for $Z = 4$. The structure was solved by the heavy atom method and refined by iterative Fourier and least squares analysis to final residuals of $R_1(F)$ 4.1% and $R_2(F)$ 6.2% for the 2550 independent reflections with $I > 2\sigma(I)$.

The Rh—P bonds of 2.354(1) Å are typical of such ligands when disposed *trans* to one another. The Rh—Cl bonds which measure 2.472(1) Å are significantly longer than normally observed due to the strong *trans* influence of the propenyl carbon atoms. The C(1)—C(2) bond measures 1.404(5) Å and is lengthened from its 1.373(5) Å value in the free $C_3Ph_3^+$ cation [9] but compares favorably to the C—C bond distances (1.36—1.46 Å) observed in other triphenylpropenyl and cyclopropenyl complexes [8, 10]. The Rh—C(1) bond of 2.000(4) Å is indicative of little if any d_π—p_π bonding. The greatest angular distortion from octahedral symmetry around the rhodium atom is associated with the chelate bite of the propenyl ligand; the C(1)—Rh—C(1)′ angle is only 65.3(2)° while the C(1)· · ·C(1)′ non-bonding distance measures 2.156(6) Å. The Rh—C(1)—C(2) and C(1)—C(2)-C(1)′ angles are 97.2(3)° and 100.3(5)°, respectively.

We have investigated this reaction further and have found that a change of counterion from Cl^- to a non-coordinating one, such as PF_6^-, also leads under identical reaction conditions to decarbonylation of $Rh(CO)Cl(PMe_2Ph)_2$ to generate a similarly colored but different complex which is believed to be $[RhCl(PMe_2Ph)_2(C_3Ph_3)][PF_6]$. This observation suggests that the loss of CO may not be initiated by nucleophilic attack of Cl^- ion on the $[Rh(CO)Cl(PMe_2Ph)_2(C_3Ph_3)]^+$ cation and raises the question as to why the rhodium complex decarbonylates while the iridium complex does not.

These are unexpected results in view of the fact that oxidative addition reactions of *trans*-$M(CO)X(PR_3)_2$ (M = Rh, Ir) usually proceed without ligand elimination to give similar products where the only difference noted is in the reaction rate (Ir faster than Rh [11]). At the present time we are attempting to characterize definitively the PF_6^- complex and are planning kinetic studies to further investigate the mechanisms of these unusual oxidative addition—ligand elimination reactions.

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