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Bridge-splitting Reactions of Rhodium Carbonyl Chloride with Monomeric and Polymeric Ligands

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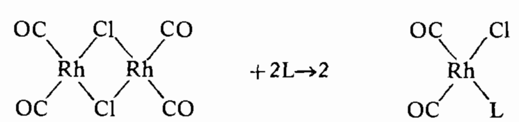
Bridge-splitting reactions of $[Rh(CO)_2Cl]_2$ *with ion exchange resin, polymer ligands were studied by comparing infrared spectra of the resultant polymer complexes with those of the monomeric analogs. In general, the complexes* cis–$Rh(CO)_2(L)Cl$, *were initially obtained. In the case of L = monomeric phosphine, these complexes had previously eluded detection.*

With L = amines, a sequence of further reactions of the cis–*dicarbonyls under high pressures of CO and* H_2 *could be followed through various rhodium carbonyl anion clusters. The position, previously unknown, of the species,* $Rh_3(CO)_{10}^-$, *in the reductive sequence of carbonyl anions was established.*

Introduction

The dimer, $[Rh(CO)_2Cl]_2$, has occasioned a good deal of recent interest. Complexes obtained from the dimer by treatment with donor ligands such as phosphines and, in fact, the dimer itself find use as catalysts in olefin hydroformylation,[1] in quadricyclene valence isomerization,[2] and in the carbonylation of methanol to acetic acid,[3] for example.

The chloride bridges in the dimer are readily split by complexing agents according to the reaction:



Known to date are the reactions where L is chloride,[4] nitrile,[5] pyridine, ammonia, and certain primary amines,[6,7] although the reports are conflicting in these last cases. The tertiary amine, Ph_3N, does not react with the dimer.[6] Thiols replace the chloride, but the dimeric structure is retained.[8]

With phosphines a further reaction occurs. The *cis*-intermediate has been postulated,[9] but the product obtained is the bis-phosphine, $Rh(Ph_3)_2(CO)Cl$. A *trans*–dicarbonyl isomer, $Rh(Ph_3)(CO)_2Cl$, has been reported recently,[10] but the *cis*–monomer has thus far eluded detection.

The preparation of a new class of insoluble catalysts, in which the metal is coordinated to a matrix-bonded ligand, such as an ion exchange resin,[11,12] has provided the incentive to investigate in more detail the bridge-splitting interaction of the rhodium carbonyl chloride dimer with donor molecules. The equilibria involved are felt to be pertinent to the understanding and control of such properties as catalyst activity and, in the case of hydroformylation, selectivity to linear and branched product.

Experimental Section

Materials. Reagent grade solvents were used throughout these investigations. Tertiary amines (Aldrich) were fractionally distilled under nitrogen before use. $Rh_2(CO)_4Cl_2$ was prepared by heating $RhCl_3 \cdot 3H_2O$ (40.00% Rh, Matthey Bishop) in a CO stream.[13] Phosphine monomers (Strem) were stored and handled under argon. Triphenylphosphine oxide was prepared from triphenylphosphine and t–butyl hydroperoxide.

Resins used (Rohm and Haas and Ionac) were: A21, poly-N,N-dimethylvinylbenzylamine); A26, poly(N,N,-N-trimethylvinylbenzylammonium)chloride and acetate; A29, poly(N-2-ethanol-N,N-dimethylvinylbenzylammonium) chloride and acetate; PVPy, poly-2-vinylpyridine; PBSH, polyvinylbenzylthiol; $PPBu_2$, poly(dibutylstyrylphosphine); and PBCN, polyvinylbenzyicyanide. The last two resins, $PPBu_2$ and PBCN, were supplied by Dr. D. D. Whitehurst. All resins used were porous, macroreticular polymers.

Monomer complexes were prepared by mixing solutions of rhodium dimer (typically 10^{-2}–10^{-3} *M*) with aliquots of a ligand-containing solution. A CO stream was passed continuously through the solution during mixing, and all solvents were saturated with CO prior to rhodium or ligand addition.

Resin complexes were prepared in an analogous

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Table I. Carbonyl Stretching Frequencies (cm^{-1}) of N-donor adducts of $[Rh(CO)_2Cl]_2$

Ligand	CO Stretch [a]					Assignment
None	2105w	2090	2080vw	2035	2005vw	
Et_3N		2090		2002		*cis*-$Rh(CO)_2(Et_3N)Cl$
DMBA		2088		2004		*cis*-$Rh(CO)_2(DMBA)Cl$
A21 Resin		2083		2002		*cis*-$Rh(CO)_2(A21)Cl$
A21 Resin [b]		2065	2040m	1995	1780mb	*cis*-$Rh(CO)_2Cl_2^- + Rh_{12}(CO)_{30}^{2-}$
A21·HCl or A26Cl		2068		1998		*cis*-$Rh(CO)_2Cl_2^-$
Pyridine		2089		2005		*cis*-$Rh(CO)_2(py)Cl$
PVPy Resin		2085		2010		*cis*-$Rh(CO)_2(PVPy)Cl$
CH_3CN[c]		2090		2020		*cis*-$Rh(CO)_2(CH_3CN)Cl$
$PhCH_2CN$ (Ref. 5)		2090		2038		*cis*-$Rh(CO)_2(PhCH_2CN)Cl$
PBCN Resin		2088		2018		*cis*-$Rh(CO)_2(PBCN)Cl$

[a] Monomers in CO-saturated hexane or benzene solution, 1 : 1 ligand/Rh. All strong, sharp bands unless otherwise noted. [b] After addition of methanol. [c] Excess nitrile; slow decomposition.

manner by the addition of rhodium dimer solution to a CO-sparged suspension of the polymer. The resultant resins typically contained 1-5% rhodium.

Instrumentation. IR data were obtained on a Beckman IR-10 spectrophotometer. For studies of liquids and mulls under pressure, an infrared cell was constructed according to the design of Noack.[14] Sodium chloride and KBr plates were used. Proton nmr spectra were measured on a Varian A-60 instrument.

Results

N-Donors. Infrared carbonyl stretching frequencies for the rhodium carbonyl chloride complexes with various monomeric and polymeric nitrogen-donor ligands are compared in Table I. Stoichiometric amounts of pyridine, triethylamine and N,N-dimethylbenzylamine (DMBA) reacted essentially quantitatively with the rhodium dimer to split the chloride bridge. The initial product of the reaction was the *cis*–$Rh(CO)_2LCl$ complex.

With the amines further reaction with dissolved CO was observed, however, and attributed to moisture in the solvent mixture. When $[Rh(CO_2)Cl]_2$ (0.02 *M*) was added to a CO-saturated benzene solution 1 *M* in Et_3N and 0.05 *M* in water, gas buret studies showed a slow net absorption of about 0.5 moles CO per mole Rh. Infrared spectra identified the $Rh_{12}(CO)_{30}^{2-}$ anion in the ill-defined solid product,[15] along with $Rh(CO)_2Cl_2^-$. Such species were to be expected from the extensive studies of Chini and Martinengo.[15,16]

The data obtained with the polymeric amine, A21, are also included in Table I. Even when moisture was carefully excluded from the reaction system, the product initially obtained from hexane or benzene solutions of the rhodium dimer was always the anion, $Rh(CO)_2Cl_2^-$. This was attributed to an ammonium ion «impurity» within the resin, an impurity arising either from inadvertent additional crosslinking in the reaction of chloromethylated polystyrene with dimethylamine or from a trimethylamine contaminant in the Rohm & Haas preparation of the resin. The identification of the $Rh(CO)_2Cl_2^-$ anion was supported by (a) converting the A21 resin to its HCl adduct prior to reaction with the rhodium dimer and (b) substituting the quaternary ammonium resins, A26 and A29, in their chloride forms for A21. Both resins, when treated with solutions of $Rh_2(CO)_4Cl_2$, showed spectra identical to those attributed to $Rh(CO)_2Cl_2^-$.

When the A21 amine resin was exhaustively washed with aqueous nitrate solution and dried azeotropically with benzene, the results presented in Table I were obtained. Reaction with $[Rh(CO)_2Cl]_2$ yielded the resin-bonded complex, *cis*–$Rh(CO)_2(A21)Cl$. This complex is, just as are the monomers, relatively unstable towards moisture. Addition of moist methanol to CO-saturated benzene suspensions of the resin caused a marked change in the IR spectrum. The rhodium amine complex was partially transformed into a mixture of $Rh(CO)_2Cl_2^-$ and small amounts of the $Rh_{12}(CO)_{30}^{2-}$ species. On addition of water the transformation was complete.

All of the results presented above were obtained under one atmosphere CO pressure at room temperature. Under higher pressures of CO, and CO/H_2 mixtures, at elevated temperatures, further reactions occur. Spectra of amine resin complexes obtained after treatment at 100°C, 1000 psig 1:1 CO/H_2, and mulled with minimal air-exposure showed bands at 2066, 1995, and 1835 cm^{-1} in varying relative intensities. These bands are assigned to $Rh(CO)_2Cl_2^-$, 2066 and 1996, and $Rh_3(CO)_{10}^-$, 1993, 1843, and 1831.[16] The cation in these resins is thought to be A21·H^+.

In order to avoid air exposure, Fluorolube and nujol mulls of the catalyst were placed in a high pressure IR cell.[14] Structural assignments were based on the work of Chini and co-workers.[16]

Under 1000 psig CO or 1:1 H_2/CO at room temperature, the $Rh(CO)_2(A21)Cl$ complex was converted into a mixture of the anionic species, $Rh(CO)_2Cl_2^-$, $Rh_3(CO)_{10}^-$, and $Rh_{12}(CO)_{30}^{2-}$. Substituting deuterium for hydrogen did not affect the spectra. On heating the IR cell to 100°C the dichloride anion bands slowly disappeared, the $Rh_3(CO)_{10}^-$ spectrum increased in intensity, and a fourth anion, $Rh_7(CO)_{16}^{3-}$, was observed. It was not possible, however, to extend this reduction to the tetracarbonylrhodate species under the accessible pressure and temperature conditions.

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Table II. Carbonyl Stretching Frequencies (cm^{-1}) of P- and S-donor Adducts of $[Rh(CO)_2Cl]_2$.

Ligand [a]	CO Stretch [b]	Assignment
PPh_3	2093 2009	*cis*-$Rh(CO)_2(PPh_3)Cl$
$PMePh_2$	2092 2008	*cis*-$Rh(CO)_2(PMePh_2)Cl$
PEt_2Ph	2096 2009	*cis*-$Rh(CO)_2(PEt_2Ph)Cl$
(Ph_3PO)	2084 2005	*cis*-$Rh(CO)_2(Ph_3PO)Cl$
Diphos	2010	Rh(CO) (Diphos)Cl
$PPBu_2$Resin		*cis*-$Rh(CO)_2(PPBu_2)Cl$
$PPBu_2$ Resin [c]	1960 - 1970	{*trans*-$Rh(CO)_2(PPBu_2)Cl$}
PrSH [d]	2075 2055 1998m	$[Rh(CO)_2(PrS)]_2$
PBSH Resin	2070m 2055 2022	{$Rh_2(CO)_4Cl(PBS)$}

[a] 1:1 Ligand/rhodium. [b] Monomers in methylene chloride, cm^{-1}, strong unless noted. [c] After treatment with 1000 psig 1:1 CO/H_2 at 100°C. [d] Excess PrSH.

P- and S- Donors. A comparison of the infrared spectra of monomeric and polymeric P- and S-donor adducts of $Rh_2(CO)_4Cl_2$ is made in Table II. On careful addition of stoichiometric amounts of various phosphine monomers to CH_2Cl_2 solutions of the carbonyl chloride (Rh/P = 1) under CO, it was possible to obtain evidence for the *cis*-isomer, $Rh(CO)_2(PR_3)Cl$. Gas buret studies showed that no CO was evolved on addition of one mole phosphine per mole rhodium. On addition of a second molar proportion f phsphine, one mle CO was evolved per Rh and the of phosphine, one mole CO was evolved per Rh and the *trans*–$Rh(CO)(PR_3)_2Cl$ was formed. *cis*-dicarbonyl[10] was the result of the limited solubility of the bis-phosphine in benzene. Attempts to isolate this intermediate by cooling or evaporating the CH_2Cl_2 solvent were unsuccessful, however, also the result of a disproportionation reaction. The facile equilibrium was demonstrated by the reaction of $Rh(CO)(Ph_3)_2Cl$ and $Rh_2(CO)_4Cl_2$ under CO. When solutions were combined in a 2:1 mole ratio, IR spectra showed that the *cis*–$Rh(CO)_2(Ph_3)Cl$ complex was formed.

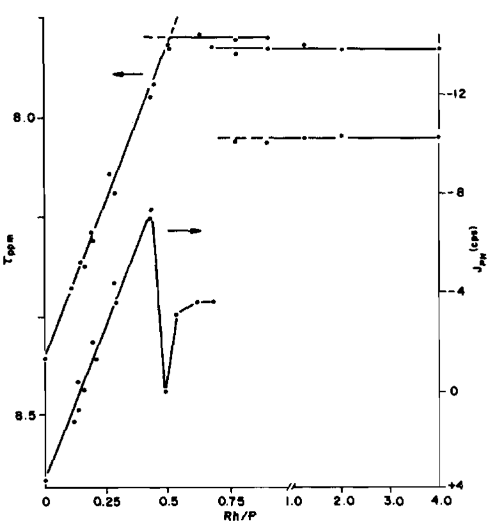
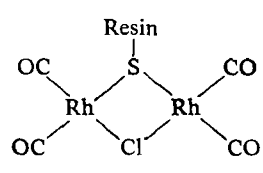


Figure 1. Chemical shifts (vs. TMS) and apparent coupling constants $Rh_2(CO)_4Cl_2$ titration with methyldiphenylphosphine in CH_2Cl_2.

Proton nmr evidence of the formation of the monophosphine intermediate was also obtained (Figure 1). Methylphenylphosphine was used. When up to one mole phosphine was present per mole rhodium, the methyl proton spectrum consisted of two doublets (τ = 7.88 ppm, J_{P-CH_3} ~10.2 cps, $J_{Rh-P-CH_3}$ ~1.1 cps). Above a P/Rh ratio of one, a new spectrum, that of *trans*–$Rh(CO)(PCH_3Ph_2)_2Cl$, is observed.[17]

With the $PPBu_2$ phosphine resin, on careful exclusion of excess chloride, evidence was obtained for initial formation of the polymer phosphine analog of *cis*–$Rh(CO)_2(PR_3)Cl$, Table II. This species, as expected, was unstable in the presence of high CO and H_2 pressures. When treated with 1000 psig 1:1 CO/H_2 at 100°C, a resin complex was isolated showing only a single CO stretching frequency at 1960-1970 cm^{-1}. Due to resin structural constraints, the crosslinking species, *trans*–$Rh(CO)(PPBu_2)_2Cl$, is thought unlikely. Instead, the assignment, *trans*–$Rh(CO)_2(PPBu_2)Cl$, analogous to the species isolated by Belluco and co-workers,[10] is made.

Both monomeric and polymeric thiols replace the bridging chloride. Due to differences in the relative intensities of the three bands observed, however, a non-crosslinking $Rh_2(CO)_4(PPBS)Cl$ complex is postulated in the resin; a disubstituted $[Rh(CO)_2(PrS)]_2$ species, in the case of the monomer thiol.[8] The structure of this resin complex is shown below.



Discussion

Bridge-spliting reactions of $Rh_2(CO)_4Cl_2$ with soluble and polystyrene-bonded donors show surprising variety, both in the similarities and in the differences between monomer and polymer ligands. With the tertiary amines, Et_3N and DMBA, simple, benzene-soluble *cis*–$Rh(CO)_2(L)Cl$ complexes were readily obtained. On treatment with CO in the presence of traces of water, carbonyl anion aggregates such as those isolated by Chini[15] precipitated.

By the use of amine resin polymers, it was possible to follow several of the successive transformations of

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these *cis*-dicarbonyl complexes under conditions of increasing CO and H_2 pressures. Under increasingly severe conditions, the simple *cis*-dicarbonyl was converted successively into $Rh_{12}(CO)_{30}^{2-}$, $Rh_3(CO)_{10}^{-}$, $Rh_7(CO)_{16}^{3-}$. From these results, then, the position of the species, $Rh_3(CO)_{10}^{-}$, in the reduction sequence of rhodium carbonyl anions[16] was established.

With soluble phosphines IR and NMR data provided strong evidence for the *cis*–$Rh(CO)_2(PR_3)Cl$. Once the existence of this mono-phosphine complex was established, the IR bands observed with polymeric phosphine resins could be explained. When contacted with high pressures of CO and H_2, the resin complex was converted to a species showing a single IR band, attributed to the structure *trans*–$Rh(CO)_2(PPBu_2)Cl$. In contrast to the amine resins, the phosphines showed no evidence of rhodium carbonyl anion formation. Since the ligand may play an important role in processes such as hydroformylation,[1] these differences should be reflected in the catalytic properties of these two materials, as is indeed the case.[12]

Conclusions

Based on comparison with monomer N-, P, and S-donors, bridge-splitting reactions of $[Rh(CO)_2Cl]_2$ with ion exchange resin analogs of the ligands were investigated. *Cis*–$Rh(CO)_2$(resin)Cl complexes were identified for both tertiary amine and phosphine polymers. The evidence supports a $[Rh_2(CO)_4$(resin)Cl] species in the case of thiol resins.

With the amine resin species, a complex series of transformations between various rhodium carbonyl anions, under high pressures of CO and H_2, could be very simply followed within the resin phase. No such series was observed with the phosphine polymers.

IR and NMR evidence for the complex, *cis*–$Rh(CO)_2(PR_3)Cl$, previously only postulated as an intermediate in the reaction of the carbonyl with phosphine, was obtained. From this evidence the IR bands observed with phosphine polymer analogs could be assigned.