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NEW RHODIUM COMPLEXES CONTAINING CYANOOLEFINS

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SUMMARY

The *trans*-[Rh(CO)L_2Cl] complexes with L=$S(C_2H_5)_2$, $Se(C_2H_5)_2$, and $Te(C_2H_5)_2$ react with tetracyanoethylene (TCNE) and fumaronitrile (FMN) to form 1/1 adducts of the formula [Rh(CO)L_2Cl(TCNE)] or [Rh(CO)L_2Cl(FMN)], in which the cyanoolefins are bonded to the metal through the olefinic bond.

The effect of the σ-donor ability of neutral ligand L on the metal→cyanoolefin π-bond is considered, and the borderline between the cyanoolefins able to form the adducts and those which are not is defined.

INTRODUCTION

We have already reported the preparation of the new halocarbonylrhodium(I) complexes *trans*-[Rh(CO)L_2Cl], where L=$S(C_2H_5)_2$, $Se(C_2H_5)_2$ and $Te(C_2H_5)_2$, and described some of their oxidative addition reactions with Cl_2, Br_2, I_2, HCl, CH_3I, and $C_6H_5SO_2Cl$[1]. We have now examined their reactions with electronegative olefins.

EXPERIMENTAL

The *trans*-[Rh(CO)L_2Cl] complexes were prepared as previously described[1]. Reagent grade tetracyanoethylene (TCNE) was purified by sublimation before use. Fumaronitrile (FMN), cinnamonitrile, and acrylonitrile were all reagent grade commercial materials.

All the reactions were carried out at room temperature and monitored by IR spectra. Elemental analyses were by Alfred Bernhardt, Microanalytisches Laboratorium, Mülheim, Germany. IR spectra were recorded on a Perkin–Elmer model 457 spectrometer.

Reaction of TCNE with trans-[Rh(CO)L_2Cl] complexes

Chlorocarbonylbis(diethyl sulphide)(tetracyanoethylene)rhodium, {Rh(CO)[$S(C_2H_5)_2$]$_2$Cl(TCNE)}, was obtained by adding a small excess of TCNE in benzene to a solution of *trans*-{Rh(CO)[$S(C_2H_5)_2$]$_2$Cl} in pentane with vigorous stirring. A yellow precipitate formed immediately. After about 30 min, the solution was concentrated, and the precipitate filtered off and washed several times with diethyl ether; decomp. >100°. (Found: C, 38.11; H, 4.15; Cl, 7.92; N, 12.21. $C_{15}H_{20}ClN_4ORhS_2$ calcd.: C, 37.95; H, 4.24; Cl, 7.47; N, 11.80%.)

The yellow solids chlorocarbonylbis(diethyl selenide)(tetracyanoethylene)-

rhodium, {$Rh(CO)[Se(C_2H_5)_2]_2Cl(TCNE)$}, decomp. 119° (Found: C, 30.96; H, 3.52; Cl, 6.27; N, 9.11. $C_{15}H_{20}ClN_4ORhSe_2$ calcd.: C, 31.65; H, 3.54; Cl, 6.23; N, 9.85%.) and chlorocarbonylbis(diethyl telluride)(tetracyanoethylene)rhodium, {$Rh(CO)[Te(C_2H_5)_2]_2Cl(TCNE)$}, decomp. 120–123°, (Found: C, 27.15; H, 3.07; Cl, 5.21; N, 8.49. $C_{15}H_{20}ClN_4ORhTe_2$ calcd.: C, 27.06; H, 3.03; Cl, 5.32; N, 8.41%.) were obtained analogously.

Reaction of FMN with trans-[$Rh(CO)L_2Cl$] complexes

This was carried out as described for the TCNE reaction, but with a reaction time of 1 h. The yellow solids chlorocarbonylbis(diethyl sulphide)(fumaronitrile)-rhodium, decomp. >71° (Found: C, 36.36; H, 5.18; Cl, 8.39; N, 6.19. $C_{13}H_{22}ClN_2ORhS_2$ calcd.: C, 36.76; H, 5.22; Cl, 8.34; N, 6.59%.), chlorocarbonylbis(diethyl selenide)(fumaronitrile)rhodium, m.p. 67–69° (Found: C, 30.05; H, 4.38; Cl, 6.66; N, 5.48. $C_{13}H_{22}ClN_2ORhSe_2$ calcd.: C, 30.11; H, 4.27; Cl, 6.83; N, 5.40%.) and chlorocarbonylbis(diethyl telluride)(fumaronitrile)rhodium, decomp. >89° (Found: C, 25.36; H, 3.84; N, 4.45. $C_{13}H_{22}ClN_2ORhTe_2$ calcd.: C, 25.36; H, 3.60; N, 4.55%.) were produced.

Attempts to prepare adducts with acrylonitrile and cinnamonitrile

An excess of acrylonitrile or cinnamonitrile was added to a benzene solution of the *trans*-[$Rh(CO)L_2Cl$] complex. No reaction could be detected after 8 h of refluxing.

RESULTS AND DISCUSSION

Tetracyanoethylene (TCNE) and fumaronitrile (FMN) react with the complexes *trans*-[$Rh(CO)L_2Cl$] at room temperature in pentane/benzene solution to form stable adducts of the type [$Rh(CO)L_2Cl$ (cyanoolefin)] in quantitative yield. On the other hand, even with a large excess of the cyanoolefin no reaction occurs in the case of acrylonitrile and cinnamonitrile.

In all the adducts prepared the cyanoolefin is bonded to the metal through the olefinic carbon–carbon double bond[2]. The IR spectra (Table 1) of the adducts, in nujol mull, have a medium band at about 2215 cm^{-1} which can be attributed to the $\nu(CN)$ stretch and a band at a frequency greater than 2000 cm^{-1} which is due to the

TABLE 1

SELECTED INFRARED BANDS (cm^{-1})[a]

Compound	ν(CN)	ν(CO)
$Rh(CO)[S(C_2H_5)_2]_2Cl(TCNE)$	2222 s	2072 s
$Rh(CO)[Se(C_2H_5)_2]_2Cl(TCNE)$	2222 s	2065 s
$Rh(CO)[Te(C_2H_5)_2]_2Cl(TCNE)$	2220 s	2059 s
$Rh(CO)[S(C_2H_5)_2]_2Cl(FMN)$	2212 m	2040 s
$Rh(CO)[Se(C_2H_5)_2]_2Cl(FMN)$	2215 m	2032 s
$Rh(CO)[Te(C_2H_5)_2]_2Cl(FMN)$	2210 m	2022 s

[a] In nujol mull.

CO stretching vibration. The values of ν(CO) in the spectra of the adducts with tetracyanoethylene are always higher than these of the corresponding complexes containing fumaronitrile. This is consistent with the view that in the latter compounds there is a relatively smaller back-donation of charge from the metal to the CO group because fumaronitrile is a poorer π-acceptor and better σ-donor than tetracyanoethylene.

The metal–olefin bonding has been explained in terms of combined metal→olefin π-bond and olefin→metal σ-bond[3]; the observation that no adducts are formed from acrylonitrile and cinnamonitrile under the same experimental conditions indicates that the stabilizing effect of the increase in the strength of the olefin→metal σ-bond on varying the cyanoolefin in the order tetracyanoethylene, fumaronitrile, cinnamonitrile and acrylonitrile does not compensate for the destabilizing effect of the decrease in the strength of the metal→olefin π-bond. The increasing basicity of the central metal associated with the relatively high σ-donor ability of the neutral ligand L leads to more effective metal–olefin π-bonding and assists the formation of stable adducts. Thus fumaronitrile is known to form stable adducts with the complexes *cis*-$[Rh(CO)_2LCl]$ when L is pyridine or *p*-toluidine but not when L is triphenylphosphine[4], while the complex *trans*-$[Rh(CO)L_2Cl]$ forms adducts with tetracyanoethylene[5] but not with fumaronitrile[6] when L is triphenylphosphine. On the other hand, fast and quantitative reactions occur with both cyanoolefins when L is diethyl sulphide, diethyl selenide, or diethyl telluride.

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